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DUVERT, Patrice etc

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(54) Title: FUNGICIDE COMPOSITIONS FOR PROTECTING FRUITS (54) Titre: COMPOSITIONS FONGICIDES POUR LA PROTECTION DES FRUITS (57) Abstract <p>The invention concerns fungicide compositions useful for fighting against phytopathogenic fungi infesting or capable of infesting fruits, containing: a) at least a fungicide compound inhibiting mitochondrial respiration; and b) at least a fungicide compound inhibiting sterol biosynthesis. The invention also concerns a method for treating fruits against fungal diseases using said compositions.</p> (57) Abrégé <p>Compositions fongicides utiles pour lutter contre les champignons phytopathogènes infestant ou susceptibles d'infester les fruits, contenant: a) au moins un composé fongicide inhibiteur de la respiration mitochondriale, et b) au moins un composé fongicide inhibiteur de la biosynthèse des stérols, et procédé de traitement des fruits contre les maladies fongiques au moyen des dites compositions.</p>		

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Compositions fongicides pour la protection des fruits

[001] La présente invention concerne de nouvelles compositions fongicides utiles dans le traitement des fruits contre les maladies fongiques, ainsi que les méthodes de traitement des fruits contre les maladies fongiques au moyen des dites compositions.

[002] Il est bien connu que les fruits, après qu'ils ont été récoltés, se recouvrent de moisissures, ce qui entraîne leur pourriture.

[003] Ces moisissures apparaissent après un temps plus ou moins long, selon la nature du fruit ou du légume et les conditions environnantes, et sont le résultat du développement de un ou plusieurs champignons phytopathogènes. Ces champignons sont pour la plupart bien connus, de même que leur mode de développement.

[004] Ainsi, de nombreuses méthodes de traitement des fruits sont déjà connues et décrites.

[005] Parmi celles-ci, on peut citer l'application par trempage et/ou brossage des fruits après récolte dans de solutions de fongicides connus. On se reportera par exemple aux travaux de A. Chitzanidis et coll., *Bulletin OEPP*, 20(1), (1990), 163-168 ou encore à ceux de E. Cohen et coll., *Phytoparasitica*, 18(1), (1990), 17-26.

[006] D'autres procédés recommandent un premier traitement de pulvérisation de composés fongicides sur les arbres fruitiers, puis une application sur les fruits par trempage et/ou brossage d'autres fongicides. Ce type de traitement est notamment décrit par S. Toker et coll., *Turk. J. Agric. For.*, 20(1), (1996), 78-83.

[007] Parmi les fongicides les plus couramment utilisés pour le traitement des fruits après récolte, on peut citer l'imazalil (décrit dans "The Pesticide Manual", 10th edition, British Crop Protection Council, page 580), le thiabendazole (*ibid.* page 972) ou encore le SOPP (o-phénylphénate de sodium, *ibid.* page 794), qui se sont avérés jusqu'à présent les plus efficaces.

[008] Ces composés sont en effet particulièrement actifs contre les souches de *Penicillium*, qui sont à l'origine de nombreuses maladies fongiques.

[009] Malheureusement, des souches de *Penicillium* résistantes au thiabendazole (P. R. Harding Jr., *Plant Dis. Rep.*, 56(3), (1972), 256-260), et plus récemment résistantes à l'imazalil sont apparues (voir par exemple les publications de J. W. Eckert, *Phytopathology*, 77(12), (1987), 1728, et *ISPP Chemical Control Newsletter*, 10, (1988), 36-38).

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[0010] Ces composés sont de plus faiblement actifs, voire inactifs sur d'autres champignons phytopathogènes. En outre, si l'imazalil peut être employé en traitement préventif et curatif, cet effet curatif reste limité dans le temps.

5 [0011] Il est également toujours souhaitable d'améliorer les produits fongicides utilisés pour traiter les fruits.

[0012] Il est également toujours souhaitable de réduire les doses de produits chimiques appliqués sur les fruits, notamment en réduisant les doses d'application des produits.

10 [0013] Il est enfin toujours désirable d'augmenter la gamme de produits antifongiques à la disposition afin de trouver parmi ceux-ci les mieux adaptés à des usages spécifiques.

[0014] Un premier objet de la présente invention consiste à fournir des compositions fongicides possédant un large spectre d'activité, c'est-à-dire possédant une activité substantielle sur un nombre de champignons phytopathogènes plus important que le
15 nombre de champignons phytopathogènes traités par les compositions connues.

[0015] Un deuxième objet de l'invention consiste à fournir des compositions fongicides possédant à la fois un effet préventif et un effet curatif, en particulier un effet curatif amélioré par rapport aux compositions fongicides actuellement utilisées.

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[0016] Un autre objet de la présente invention consiste à fournir des compositions fongicides qui parviennent à lutter efficacement contre les souches de champignons résistantes aux compositions fongicides connues.

25 [0017] Un autre but de la présente invention est de fournir des compositions fongicides qui sont efficaces à des doses substantiellement plus faibles par rapport aux doses actuellement appliquées.

30 [0018] Un autre objet de la présente invention consiste à fournir des compositions fongicides appliquées sur des fruits afin d'empêcher ou de retarder leur pourrissement, tout en restant propres à la consommation.

[0019] D'autres objets de l'invention apparaîtront dans l'exposé de l'invention qui est présenté dans la suite de la présente description.

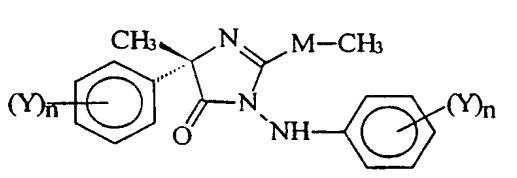
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[0020] De façon surprenante, il a été découvert que l'ensemble de ces objets est atteint en totalité ou partie grâce aux compositions fongicides objet de la présente invention.

[0021] La présente invention concerne donc des compositions fongicides utiles pour lutter contre les champignons phytopathogènes infestant ou susceptibles d'infester les fruits, caractérisée en ce qu'elles contiennent :

- au moins un composé fongicide inhibiteur de la respiration mitochondriale, et
- au moins un composé fongicide inhibiteur de la biosynthèse des stérols.

[0022] Parmi les composés fongicides inhibiteurs de la respiration mitochondriale, on peut citer par exemple la strobilurine et dérivés ou composés analogues, comme par exemple l'azoxystrobine, le krésoxim-méthyl, la trifloxystrobine, la picoxystrobine, la discostrobine, mais aussi le 4-chloro-2-cyano-N,N-diméthyl-5-p-tolylimidazole-1-sulfonamide, la 5-méthyl-5-(4-phénoxyphényl)-3-(phénylamino)-2,4-oxazolidinedione (ou Famoxadone) ainsi que les composés de formule générale (I) :



dans laquelle :

- M représente un atome d'oxygène ou de soufre ;
- n est un nombre entier égal à 0 ou 1 ;
- Y est un atome de fluor ou de chlore, ou un radical méthyle.

[0023] Les composés de formule (I) sont connus, notamment par la demande de brevet EP-A-0 629 616.

[0024] De façon préférée, on choisira parmi les composés de formule (I), le composé pour lequel M représente un atome de soufre et n est égal à 0, c'est-à-dire la (4-S)-4-méthyl-2-méthylthio-4-phényl-1-phénylamino-2-imidazoline-5-one, dénommée, Fénamidone.

[0025] La liste des composés fongicides inhibiteurs de la respiration mitochondriale ne doit pas être considérée comme limitative, mais comme illustrant, pour l'homme du métier, la gamme de composés inhibiteurs de respiration mitochondriale dont il dispose.

[0026] De même, à titre d'illustration, parmi les composés inhibiteurs de la biosynthèse des stérols qui peuvent être utilisés dans les compositions fongicides de la présente invention, on peut citer par exemple, l'imazalil.

5 [0027] De façon préférée, on choisira, pour les compositions fongicides objet de l'invention, comme inhibiteur de respiration mitochondriale, un composé de formule (I) ou la famoxadone, et comme inhibiteur de la biosynthèse des stérols, l'imazalil.

10 [0028] De manière tout particulièrement préférée, les compositions fongicides selon la présente invention comprennent l'imazalil en association avec la fénamidone.

[0029] Les compositions selon la présente invention se présentent sous la forme de liquides plus ou moins visqueux, allant d'une viscosité semblable à celle de l'eau, d'huile, jusqu'à des formulations de type cires.

15 [0030] En règle générale, les doses des composés fongicides présents dans les compositions de l'invention dépendent de la nature des composés eux-mêmes, de la nature des fruits à traiter, ainsi que de la nature des maladies à traiter et de leur degré d'infestation.

20 [0031] Les doses d'inhibiteurs de respiration mitochondriale utilisées pour les compositions fongicides de la présente invention sont avantageusement comprises entre 10 mg/l et 1000 mg/l, de préférence comprises entre 20 mg/l et 300 mg/l, de préférence encore entre 40 mg/l et 150 mg/l, par exemple entre 50 mg/l et 100 mg/l.

25 [0032] Les doses d'inhibiteurs de biosynthèse des stérols utilisées pour les compositions fongicides de la présente invention sont avantageusement comprises entre 100 mg/l et 3000 mg/l, de préférence comprises entre 50 mg/l et 2500 mg/l, de préférence encore entre 200 mg/l et 2000 mg/l, par exemple entre environ 400 mg/l et 1000 mg/l.

30 [0033] Il est bien entendu que les compositions fongicides selon la présente invention peuvent contenir, outre un ou plusieurs inhibiteurs de la respiration mitochondriale et un ou plusieurs inhibiteurs de la biosynthèse des stérols, un ou plusieurs autres composés fongicides connus de l'homme du métier et adaptés aux traitements des maladies
35 fongiques des fruits.

[0034] À titre d'exemple non limitatif, les autres composés fongicides qui peuvent être inclus dans les compositions de l'invention, comprennent l'acide phosphoreux, ainsi que ses dérivés et ses sels. Un produit tout particulièrement adapté aux compositions de la présente invention est le sel d'aluminium de l'acide phosphoreux, dénommé Fosétyl-Al (décrit dans "The Pesticide Manual", 10th edition, British Crop Protection Council, page 530).

[0035] Ainsi, une composition tout particulièrement préférée de la présente invention comprend imazalil, fénamidone et fosétyl-Al.

[0036] Les doses de ces autres composés fongicides qui peuvent être ajoutés aux compositions selon la présente invention sont fonction des types de maladies à traiter, de leur degré d'infestation, de la nature des fruits à traiter et de la nature elle-même de ces composés. L'homme du métier saura apprécier les doses à appliquer qui pourront par exemple être comprises entre 500 mg/l et 6000 mg/l, par exemple entre 2000 mg/l et 4000 mg/l.

[0037] Lorsque le fosétyl-Al est utilisé, la dose d'emploi est généralement comprise entre 1000 mg/l et 1500 mg/l, de préférence environ 1200 mg/l.

[0038] Il a donc été découvert de façon surprenante que l'ajout d'un inhibiteur de la respiration mitochondriale à un inhibiteur de la biosynthèse des stérols augmente substantiellement le spectre d'activité des compositions fongicides et notamment possède une efficacité inattendue sur les souches de champignons phytopathogènes résistantes aux inhibiteurs de la biosynthèse des stérols.

[0039] Ainsi, les compositions fongicides selon l'invention sont efficaces pour traiter la majeure partie des champignons phytopathogènes infestant ou susceptibles d'infester les fruits et notamment :

- *Phytophthora spp.*, par exemple la pourriture brune des agrumes (*Phytophthora parasitica*), et la gommose des citrus (*Phytophthora citrophthora*) ;
- *Penicillium spp.*, par exemple la moisissure bleue (*Penicillium italicum*), et la moisissure verte (*Penicillium digitatum*) ;
- la pourriture amère des agrumes (*Geotrichum candidum*) ;
- le black-rot des agrumes (*Alternaria citri*) ;
- l'anthracnose (*Colletotrichum gloeosporioides*) ;
- la mélanose ou pourriture phomopsienne (*Diplodia natalensis* ou *Phomopsis citri*).

[0040] D'autres champignons phytopathogènes peuvent également être contrôlés à l'aide des compositions fongicides de l'invention. La nature de ces autres champignons dépend en partie de la nature des autres fongicides présents dans les compositions objet de l'invention.

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[0041] Les fruits qui peuvent être traités par les compositions selon l'invention sont de tout type, et particulièrement ceux qui peuvent être endommagés par l'apparition des champignons phytopathogènes décrits plus haut, notamment lors d'un stockage prolongé des dits fruits.

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[0042] De plus les compositions selon l'invention trouvent une utilisation particulièrement avantageuse dans le traitement des fruits après récolte, afin d'empêcher ou de retarder leur pourrissement, tout en restant propres à la consommation.

[0043] Ainsi, parmi les fruits qui peuvent être traités avec les compositions fongicides de l'invention on peut citer notamment les agrumes, par exemple, citrons, oranges,

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pamplemousses, cédrats, clémentines, mandarines, etc.

[0044] Il apparaît ainsi que le champ d'application des compositions fongicides décrites ici n'est pas limité, et que ces compositions peuvent être employées dans tous les cas de figure où une protection ou une action contre les attaques fongiques est nécessaire afin d'empêcher ou d'enrayer le pourrissement de fruits comestibles.

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[0045] Les compositions selon l'invention comprennent, outres les composés fongicides décrits auparavant, les supports solides ou liquides, acceptables dans le traitement fongique des fruits et/ou les agents tensioactifs également acceptables dans le traitement fongique des fruits. En particulier sont utilisables les supports inertes et usuels et les agents tensioactifs usuels. Ces compositions recouvrent non seulement les compositions prêtes à être appliquées sur les fruits à traiter par trempage ou au moyen d'un dispositif adapté, mais également les compositions concentrées commerciales qui doivent être diluées avant application sur les fruits.

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[0046] Ces compositions fongicides selon l'invention peuvent contenir aussi toute sorte d'autres ingrédients tels que, par exemple, des colloïdes protecteurs, des adhésifs, des épaississants, des agents thixotropes, des agents de pénétration, des stabilisants, des séquestrants, des agents de texture, des agents de saveur, des exhausteurs de goût, des sucres, des édulcorants, des colorants, etc... Plus généralement, les matières actives peuvent être combinées à tous les additifs solides ou liquides correspondant aux techniques habituelles de la mise en formulation.

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[0047] D'une façon générale, les compositions selon l'invention contiennent habituellement de 0,05 à 95 % (en poids) de matière active (par matière active, on entend ici l'ensemble des composés fongicides compris dans la présente formulation), un ou plusieurs supports solides ou liquides et, éventuellement, un ou plusieurs agents tensioactifs.

[0048] Par le terme "support", dans le présent exposé, on désigne une matière organique ou minérale, naturelle ou synthétique, avec laquelle la matière active est combinée pour faciliter son application sur les fruits. Ce support est donc généralement inerte et il doit être acceptable dans le domaine agro-alimentaire. Le support peut être solide (argiles, silicates naturels ou synthétiques, silice, résines, cires, engrais solides, etc...) ou liquide (eau, alcools, notamment le butanol, etc...).

[0049] L'agent tensioactif peut être un agent émulsionnant, dispersant ou mouillant de type ionique ou non ionique ou un mélange de tels agents tensioactifs. On peut citer par exemple des sels d'acides polyacryliques, des sels d'acides lignosulfoniques, des sels d'acides phénolsulfoniques ou naphthalènesulfoniques, des polycondensats d'oxyde d'éthylène sur des alcools gras ou sur des acides gras ou sur des amines grasses, des phénols substitués (notamment des alkylphénols ou des arylphénols), des sels d'esters d'acides sulfosucciniques, des dérivés de la taurine (notamment des alkyltaurates), des esters phosphoriques d'alcools ou de phénols polyoxyéthylés, des esters d'acides gras et de polyols, les dérivés à fonction sulfates, sulfonates et phosphates des composés précédents. La présence d'au moins un agent tensioactif est généralement indispensable lorsque la matière active et/ou le support inerte ne sont pas solubles dans l'eau et que l'agent vecteur de l'application est l'eau.

[0050] Ainsi donc, les compositions selon l'invention peuvent contenir la matière active dans de très larges limites, allant de 0,05 % à 95 % (en poids). Leur teneur en agent tensioactif est avantageusement comprise entre 0,5 % et 40 % en poids. Sauf indication contraire les pourcentages donnés dans cette description sont des pourcentages pondéraux.

[0051] Ces compositions selon l'invention sont elles-mêmes sous des formes assez diverses, solides ou liquides.

[0052] Comme formes de compositions solides, on peut citer les poudres pour poudrage (à teneur en matière active pouvant aller jusqu'à 100 %) et les granulés, notamment ceux obtenus par extrusion, par compactage, par imprégnation d'un support granulé, par

granulation à partir d'une poudre (la teneur en matière active dans ces granulés étant entre 0,5 et 80 % pour ces derniers cas). De telles compositions solides peuvent éventuellement être mises sous forme liquide plus ou moins visqueux, selon le type d'application désiré, par exemple, par dilution dans l'eau.

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[0053] Comme formes de compositions liquides ou destinées à constituer des compositions liquides lors de l'application, on peut citer les solutions, en particulier les concentrés solubles dans l'eau, les émulsions, les suspensions concentrées, les poudres mouillables (ou poudre à pulvériser), les huiles et les cires.

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[0054] Les suspensions concentrées, applicables en pulvérisation, sont préparées de manière à obtenir un produit fluide stable ne se déposant pas et elles contiennent habituellement de 10 à 75 % de matière active, de 0,5 à 15 % d'agents tensioactifs, de 0,1 à 10 % d'agents thixotropes, de 0 à 10 % d'additifs appropriés, comme des anti-mousses, des inhibiteurs de corrosion, des stabilisants, des agents de pénétration et des adhésifs et, comme support, de l'eau ou un liquide organique dans lequel la matière active est peu ou pas soluble : certaines matières solides organiques ou des sels minéraux peuvent être dissous dans le support pour aider à empêcher la sédimentation ou comme antigels pour l'eau.

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[0055] A titre d'exemple, voici une composition de suspension concentrée :

Exemple SC 1 :

	• - matière active	500 g
	• - phosphate de tristyrylphénol polyéthoxylé	50 g
25	• - alkylphénol polyéthoxylé	50 g
	• - polycarboxylate de sodium	20 g
	• - éthylène glycol	50 g
	• - huile organopolysiloxanique (antimousse)	1 g
	• - polysaccharide	1,5 g
30	• - eau	316,5 g

[0056] Les poudres mouillables (ou poudre à pulvériser) sont habituellement préparées de manière qu'elles contiennent 20 à 95 % de matière active, et elles contiennent habituellement, en plus du support solide, de 0 à 30 % d'un agent mouillant, de 3 à 20 % d'un agent dispersant, et, quand c'est nécessaire, de 0,1 à 10 % d'un ou plusieurs stabilisants et/ou autres additifs, comme des agents de pénétration, des adhésifs, ou des agents antimottants, colorants, etc...

[0057] Pour obtenir les poudres à pulvériser ou poudres mouillables, on mélange intimement les matières actives dans les mélangeurs appropriés avec les substances additionnelles et on broie avec des moulins ou autres broyeurs appropriés. On obtient par-là des poudres à pulvériser dont la mouillabilité et la mise en suspension sont avantageuses ; on peut les mettre en suspension avec de l'eau à toute concentration désirée et ces suspensions sont utilisables très avantageusement en particulier pour l'application par exemple sur les feuilles des végétaux ou sur les semences.

[0058] A titre d'exemple, voici une composition pour poudre mouillable (ou poudre à pulvériser) :

Exemple PM 1

	• - matière active	50%
15	• - alcool gras éthoxylé (agent mouillant)	2,5%
	• - phényléthylphénol éthoxylé (agent dispersant)	5%
	• - farine (support inerte)	42,5%

[0059] Les dispersions et émulsions aqueuses, par exemple les compositions obtenues en diluant à l'aide d'eau une poudre mouillable selon l'invention, sont comprises dans le cadre général de la présente invention. Les émulsions peuvent être du type eau-dans-l'huile ou huile-dans-l'eau et elles peuvent avoir une consistance épaisse comme celle d'une "mayonnaise", voire d'une cire.

[0060] Les compositions fongicides selon l'invention peuvent être formulées sous la forme de granulés dispersables dans l'eau également compris dans le cadre de l'invention.

[0061] Ces granulés dispersables, de densité apparente généralement comprise entre environ 0,3 et 0,6 ont une dimension de particules généralement comprise entre environ 150 et 2000 et de préférence entre 300 et 1500 microns.

[0062] La teneur en matière active de ces granulés est généralement comprise entre environ 1 % et 90 %, et de préférence entre 25 % et 90 %.

[0063] Le reste du granulé est essentiellement composé d'une charge solide et éventuellement d'adjuvants tensioactifs conférant au granulé des propriétés de dispersibilité dans l'eau. Ces granulés peuvent être essentiellement de deux types distincts selon que la charge retenue est soluble ou non dans l'eau. Lorsque la charge est hydrosoluble, elle peut être minérale ou, de préférence, organique. Dans le cas d'une

charge insoluble, celle-ci est de préférence minérale, comme par exemple le kaolin ou la bentonite. Elle est alors avantageusement accompagnée d'agents tensioactifs (à raison de 0,5 à 20 % en poids du granulé) dont plus de la moitié est, par exemple, constituée par au moins un agent dispersant, essentiellement anionique, tel qu'un polynaphtalène sulfonate alcalin ou alcalino-terreux ou un lignosulfonate alcalin ou alcalino-terreux, le reste étant constitué par des mouillants non ioniques ou anioniques tel qu'un alcoylnaphtalène sulfonate alcalin ou alcalino-terreux.

[0064] Par ailleurs, bien que cela ne soit pas indispensable, on peut ajouter d'autres adjuvants tels que des agents anti-mousse.

[0065] Le granulé selon l'invention peut être préparé par mélange des ingrédients nécessaires puis granulation selon plusieurs techniques en soi connues (drageoir, lit fluide, atomiseur, extrusion, etc.). On termine généralement par un concassage suivi d'un tamisage à la dimension de particule choisie dans les limites mentionnées ci-dessus. On peut encore utiliser des granulés obtenus comme précédemment puis imprégnés avec une composition contenant la matière active.

[0066] De manière tout à fait avantageuse, les compositions selon la présente invention sont adaptées pour une application, sur les fruits à traiter, par pulvérisation, par trempage, par pelliculage, par enrobage, etc.

[0067] La présente invention concerne également un procédé de traitement des fruits, caractérisé en ce qu'on l'on traite les fruits avec une composition fongicide selon l'invention, par trempage, pulvérisation, brossage, enrobage, pelliculage, etc. Ces techniques de traitement sont bien connues de l'homme du métier.

[0068] À titre d'exemple, le traitement par trempage consiste à tremper directement les fruits dans une solution aqueuse d'une composition fongicide selon l'invention. Cette opération peut être effectuée manuellement ou mécaniquement.

[0069] Un traitement mécanique particulièrement préféré est le brossage, c'est-à-dire que les composés fongicides sont appliqués à l'aide de brosses situées, par exemple, au-dessus de rouleaux sur lesquels se déplacent les fruits.

[0070] D'autres techniques, comme la pulvérisation au moyen d'appareils munis de buses, ou encore le pelliculage ou l'enrobage, dans des cylindres ou des "bétonnières" munis ou non de rouleaux, de brosses et/ou de pas de vis, font appel à des techniques connues qui ne seront pas développées ici.

[0071] Il est à noter que le traitement des fruits à l'aide des compositions fongicides selon l'invention est effectué de préférence après la récolte, de manière préventive et/ou curative, c'est-à-dire avant et/ou après qu'une maladie ne soit apparue sur les fruits
5 traités.

[0072] Les composés fongicides compris dans les compositions selon l'invention peuvent être appliqués sur les fruits de manière simultanée, séquencée ou séparée.

[0073] De plus, le traitement avec les compositions fongicides selon l'invention est compatible avec un traitement pré-récolte classique, ce traitement pouvant être de tout
10 type connu, fongicide et/ou insecticide.

[0074] Un tel traitement fongicide et/ou insecticide combiné avec un traitement, de préférence après récolte, avec une ou plusieurs compositions fongicides selon la présente invention est également compris dans le champ de la présente invention.

[0075] Enfin, la présente invention concerne également les fruits traités par une ou
15 plusieurs compositions selon la présente invention.

[0076] Les exemples suivants sont donnés à titre non limitatifs dans le seul but de montrer l'excellente efficacité des compositions selon l'invention, et de montrer
20 comment elles sont mises en œuvre.

Exemple 1 (action curative) :

Sur des citrons, une petite zone du zeste a été enlevée (de l'ordre de 1 cm²). Après avoir
25 réalisé cette opération, une inoculation par une suspension de spores de *Penicillium digitatum* (concentration 3.900.000 spores/ml) à raison de 5 gouttes par fruit a été effectuée à l'endroit où le zeste a été enlevé. Les citrons, à raison de 3 fruits/facteur d'essai, ont été placés dans des coupelles, ensachés et mis en incubation à 20°C pendant 24 heures. Après ce délai, un traitement fongicide par pulvérisation a été pratiqué. Les
30 produits et doses employées ont été les suivants :

- Composition de référence A : fénamidone + fosétyl-Al aux doses de 17 + 250, 33 + 500, 66 + 1000, 133g + 2000 mg de matières actives par litre.

- Composition de référence B : imazalil (formulation commerciale Deccosil Agrumes*, concentré émulsionnable à 200g/l) aux doses de 125, 250, 500 et 1000 mg d'imazalil par litre.

- Exemple de composition 1 : Composition A + Composition B aux doses de (17 + 250) + 125, (33 + 500) + 250, (66 + 1000) + 500 et (133 + 2000) + 1000 mg de matières actives par litre (premier lot de doses).

5

- Exemple de composition 2 : Composition A + Composition B aux doses de (10 + 150) + 75, (20 + 300) + 150, (40 + 600) + 300 et (80 + 1200) + 600 mg de matières actives par litre (second lot de doses).

10 [0077] Après le traitement, les citrons ont été de nouveau ensachés puis replacés à 20°C pour 6 jours.

Au 6e jour après le traitement, une notation a été effectuée. Elle a consisté à déterminer le pourcentage de surface contaminée et, par comparaison à un témoin non traité et inoculé, à définir le pourcentage d'efficacité.

15

Résultats :

<i>Composition</i>	<i>Doses (mg/l) (fénamidone + fosétyl-Al) + imazalil</i>	<i>% efficacité</i>
Composition A	(17 + 250)	0
	(33 + 500)	16
	(66 + 1000)	0
	(133 + 2000)	0
Composition B	125	80
	250	32
	500	93
	1000	96
Composition 1 (Premier lot de doses)	(17 + 250) + 125	52
	(33 + 500) + 250	88
	(66 + 1000) + 500	93
	(133 + 2000) + 1000	98
Composition 2 (Second lot de doses)	(10 + 150) + 75	60
	(20 + 300) + 150	88
	(40 + 600) + 300	95
	(80 + 1200) + 600	98

Le témoin non-traité est contaminé à 83%.

Exemple 1 (action préventive) :

5 Le protocole expérimental suivi est identique au précédent mis à part le fait que le traitement est cette fois-ci effectué un jour avant l'inoculation.

Résultats :

<i>Composition</i>	<i>Doses (mg/l)</i> <i>(ffénamidone + fosétyl-Al) + imazalil</i>	<i>% efficacité</i>
Composition A	(17 + 250)	0
	(33 + 500)	11
	(66 + 1000)	0
	(133 + 2000)	39
Composition B	125	67
	250	32
	500	93
	1000	100
Composition 1 (Premier lot de doses)	(17 + 250) + 125	87
	(33 + 500) + 250	92
	(66 + 1000) + 500	98
	(133 + 2000) + 1000	100
Composition 2 (Second lot de doses)	(10 + 150) + 75	78
	(20 + 300) + 150	92
	(40 + 600) + 300	94
	(80 + 1200) + 600	100

10 Le témoin non-traité est contaminé à 30%.

[0078] Les résultats ci-dessus montrent que :

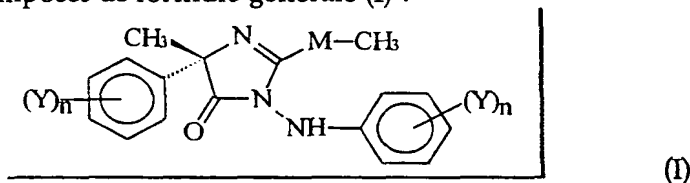
- les compositions selon l'invention possèdent une activité préventive et curative par rapport à des témoins non traités.
- les compositions selon l'invention ont une meilleure efficacité par rapport aux compositions connues, et ce même à des doses de produits comparables inférieures.

REVENDICATIONS

5 1. Compositions fongicides utiles pour lutter contre les champignons phytopathogènes infestant ou susceptibles d'infester les fruits, caractérisée en ce qu'elles contiennent :

- a) au moins un composé fongicide inhibiteur de la respiration mitochondriale, et
b) au moins un composé fongicide inhibiteur de la biosynthèse des stérols.

10 2. Compositions fongicides selon la revendication 1, caractérisées en ce que le composé fongicide inhibiteur de la respiration mitochondriale est choisi parmi l'azoxystrobine, le krésoxym-méthyl, la trifloxystrobine, la picoxystrobine, la discoxystrobine, le 4-chloro-2-cyano-N,N-diméthyl-5-p-tolylimidazole-1-sulfonamide, la
15 famoxadone et les composés de formule générale (I) :



dans laquelle :

- M représente un atome d'oxygène ou de soufre ;
- n est un nombre entier égal à 0 ou 1 ;
- Y est un atome de fluor ou de chlore, ou un radical méthyle.

25 3. Compositions fongicides selon la revendication 2, caractérisées en ce que le composé fongicide inhibiteur de la respiration mitochondriale est choisi parmi la famoxadone et un composé de formule (I) tel que défini dans la revendication 2.

4. Compositions fongicides selon l'une des revendications 2 ou 3, caractérisées en ce que le composé fongicide inhibiteur de la respiration mitochondriale est la fénamidone.

30 5. Compositions fongicides selon l'une quelconque des revendications précédentes, caractérisées en ce que le composé inhibiteur de la biosynthèse des stérols est l'imazalil.

6. Compositions fongicides selon l'une quelconque des revendications

précédentes, caractérisées en ce qu'elles comprennent l'imazalil en association avec la fénamidone.

7. Compositions fongicides selon l'une quelconque des revendications précédentes, caractérisées en ce que les doses de composés fongicides inhibiteurs de la respiration mitochondriale sont comprises entre 10 mg/l et 1000 mg/l, de préférence entre 20 mg/l et 300 mg/l, de préférence encore entre 40 mg/l et 150 mg/l, ou entre 50 mg/l et 100 mg/l.
8. Compositions fongicides selon l'une quelconque des revendications précédentes, caractérisées en ce que les doses de composés fongicides inhibiteurs de biosynthèse des stérols sont comprises entre 100 mg/l et 3000 mg/l, de préférence comprises entre 50 mg/l et 2500 mg/l, de préférence encore entre 200 mg/l et 2000 mg/l, ou entre environ 400 mg/l et 1000 mg/l.
9. Compositions fongicides selon l'une quelconque des revendications précédentes, caractérisées en ce qu'elles comprennent en outre un ou plusieurs autres composés fongicides.
10. Compositions fongicides selon la revendication 9, caractérisées en ce que l'autre composé fongicide est choisi parmi l'acide phosphoreux, ses dérivés et ses sels.
11. Compositions fongicides selon l'une des revendications 9 ou 10, caractérisées en ce que l'autre composé fongicide est le fosétyl-Al.
12. Compositions fongicides selon l'une quelconque des revendications 9 à 11, caractérisées en ce que l'autre composé fongicide est présent à des doses comprises entre 500 mg/l et 6000 mg/l, par exemple entre 2000 mg/l et 4000 mg/l.
13. Compositions fongicides selon l'une quelconque des revendications précédentes, caractérisées en ce qu'elles comprennent imazalil, fénamidone et fosétyl-Al.
14. Compositions fongicides selon l'une quelconque des revendications précédentes, caractérisées en ce qu'elles sont utiles pour traiter un ou plusieurs des champignons phytopathogènes choisis parmi :
Phytophthora spp., par exemple la pourriture brune des agrumes (*Phytophthora parasitica*), et la gommose des citrus (*Phytophthora citrophthora*) ;

Penicillium spp., par exemple la moisissure bleue (*Penicillium italicum*), et la moisissure verte (*Penicillium digitatum*) ;

la pourriture amère des agrumes (*Geotrichum candidum*) ;

le black-rot des agrumes (*Alternaria citri*) ;

5 l'anthracnose (*Colletotrichum gloeosporioides*) ; et

la mélanose ou pourriture phomopsienne (*Diplodia natalensis* ou *Phomopsis citri*).

15 15. Compositions fongicides selon l'une quelconque des revendications précédentes, caractérisées en ce qu'elles protègent ou luttent contre les attaques fongiques et empêchent ou enrayent le pourrissement de fruits comestibles.

16. Compositions fongicides selon l'une quelconque des revendications précédentes, caractérisées en ce que les fruits sont des agrumes.

15 17. Compositions fongicides selon l'une quelconque des revendications précédentes, caractérisées en ce qu'elles comprennent, outre les composés fongicides décrites dans les revendications précédentes, un ou plusieurs supports inertes solides ou liquides, agents tensioactifs, colloïdes protecteurs, adhésifs, épaississants, agents thixotropes, agents de pénétration, stabilisants, séquestrants, agents de texture, agents de
20 saveur, exhausteurs de goût, sucres, édulcorants, et/ou des colorants.

18. Compositions fongicides selon l'une quelconque des revendications précédentes, caractérisées en ce qu'elles contiennent 0,05 à 95 % en poids de matière active.

25 19. Compositions fongicides selon l'une quelconque des revendications précédentes, caractérisées en ce qu'elles sont sous forme solide ou liquide.

30 20. Procédé de traitement des fruits, caractérisé en ce qu'on l'on traite les fruits avec une composition fongicide selon l'une quelconque des revendications précédentes, par trempage, pulvérisation, brossage, enrobage, ou pelliculage des dits fruits.

21. Procédé de traitement des fruits selon la revendication 20, caractérisé en ce que le dit traitement est effectué de manière préventive et/ou curative.

35

22. Procédé de traitement des fruits selon la revendication 20, caractérisé en ce que le dit traitement est effectué après la récolte des fruits.

23. Procédé de traitement des fruits selon l'une des revendications 20 à 22, caractérisé en ce que les composés fongicides sont appliqués de manière simultanée, séquencée ou séparée.

5

24. Procédé de traitement des fruits, caractérisé en ce qu'il combine un traitement fongicide et/ou insecticide avec un traitement par une ou plusieurs compositions fongicides selon l'une quelconque des revendications 1 à 19.

10

25. Fruits traités par une ou plusieurs compositions selon la présente invention.

INTERNATIONAL SEARCH REPORT

Inte Application No

PCT/FR 00/00339

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A01N43/50 A01N57/12 A01N61/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 96 03044 A (RHONE POULENC) 8 February 1996 (1996-02-08) page 1, line 31 -page 4, line 13 examples 1,2,12,21-29 ---	1,2,4, 7-12, 14-25
X	EP 0 531 837 A (BASF) 17 March 1993 (1993-03-17) see the whole document ---	1,2,5,7, 8,14-25
X	FR 2 754 424 A (RHONE POULENC) 17 April 1998 (1998-04-17) see the whole document ---	1,2,7,8, 14,17-19
X	EP 0 524 496 A (BASF) 27 January 1993 (1993-01-27) see the whole document ---	1,2,7-9, 14-25
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search

3 April 2000

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/FR 00/00339

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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X	<p>"MIXTURES OF FUNGICIDES, INSECTICIDES AND HERBICIDES", RESEARCH DISCLOSURE, NR. 388, PAGE(S) 489/490 XP000635427 ISSN: 0374-4353 see the whole document -----</p>	<p>1-3,7-9, 14-25</p>

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. Application No

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RAPPORT DE RECHERCHE INTERNATIONALE

Den XXXXXXXXXX Internationale No
PCT/FR 00/00339

A. CLASSEMENT DE L'OBJET DE LA DEMANDE CIB 7 A01N43/50 A01N57/12 A01N61/00		
Selon la classification internationale des brevets (CIB) ou à la fois selon la classification nationale et la CIB		
B. DOMAINES SUR LESQUELS LA RECHERCHE A PORTE		
Documentation minimale consultée (système de classification suivi des symboles de classement) CIB 7 A01N		
Documentation consultée autre que la documentation minimale dans la mesure où ces documents relèvent des domaines sur lesquels a porté la recherche		
Base de données électronique consultée au cours de la recherche internationale (nom de la base de données, et si réalisable, termes de recherche utilisés)		
C. DOCUMENTS CONSIDERES COMME PERTINENTS		
Catégorie	Identification des documents cités, avec, le cas échéant, l'indication des passages pertinents	no. des revendications visées
X	WO 96 03044 A (RHONE POULENC) 8 février 1996 (1996-02-08) page 1, ligne 31 -page 4, ligne 13 exemples 1,2,12,21-29 ---	1,2,4, 7-12, 14-25
X	EP 0 531 837 A (BASF) 17 mars 1993 (1993-03-17) * voir le document entier * ---	1,2,5,7, 8,14-25
X	FR 2 754 424 A (RHONE POULENC) 17 avril 1998 (1998-04-17) * voir le document entier* ---	1,2,7,8, 14,17-19
X	EP 0 524 496 A (BASF) 27 janvier 1993 (1993-01-27) *voir le document entier* ---	1,2,7-9, 14-25
-/--		
<div style="display: flex; justify-content: space-between;"> <input checked="" type="checkbox"/> Voir la suite du cadre C pour la fin de la liste des documents <input checked="" type="checkbox"/> Les documents de familles de brevets sont indiqués en annexe </div>		
<div style="display: flex;"> <div style="flex: 1;"> <p>° Catégories spéciales de documents cités:</p> <p>"A" document définissant l'état général de la technique, non considéré comme particulièrement pertinent</p> <p>"E" document antérieur, mais publié à la date de dépôt international ou après cette date</p> <p>"L" document pouvant jeter un doute sur une revendication de priorité ou cité pour déterminer la date de publication d'une autre citation ou pour une raison spéciale (telle qu'indiquée)</p> <p>"O" document se référant à une divulgation orale, à un usage, à une exposition ou tous autres moyens</p> <p>"P" document publié avant la date de dépôt international, mais postérieurement à la date de priorité revendiquée</p> </div> <div style="flex: 1;"> <p>"T" document ultérieur publié après la date de dépôt international ou la date de priorité et n'appartenant pas à l'état de la technique pertinent, mais cité pour comprendre le principe ou la théorie constituant la base de l'invention</p> <p>"X" document particulièrement pertinent; l'invention revendiquée ne peut être considérée comme nouvelle ou comme impliquant une activité inventive par rapport au document considéré isolément</p> <p>"Y" document particulièrement pertinent; l'invention revendiquée ne peut être considérée comme impliquant une activité inventive lorsque le document est associé à un ou plusieurs autres documents de même nature, cette combinaison étant évidente pour une personne du métier</p> <p>"&" document qui fait partie de la même famille de brevets</p> </div> </div>		
Date à laquelle la recherche internationale a été effectivement achevée <div style="text-align: center; font-weight: bold;">3 avril 2000</div>		Date d'expédition du présent rapport de recherche internationale <div style="text-align: center; font-weight: bold;">11/04/2000</div>
Nom et adresse postale de l'administration chargée de la recherche internationale Office Européen des Brevets, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Fonctionnaire autorisé <div style="text-align: center; font-weight: bold;">Fort, M</div>

RAPPORT DE RECHERCHE INTERNATIONALE

er le Internationale No

PCT/FR 00/00339

C.(suite) DOCUMENTS CONSIDERES COMME PERTINENTS

Catégorie	Identification des documents cités. avec le cas échéant. l'indication des passages pertinents	no. des revendications visées
X	WO 93 22921 A (ZENECA) 25 novembre 1993 (1993-11-25) * voir le document entier* ---	1,2,7-9, 14-25
X	WO 98 33381 A (DU PONT DE NEMOURS) 6 août 1998 (1998-08-06) * voir p.12, "Preferred 6"* page 18, ligne 8 -page 19, ligne 21 page 34, ligne 6 - ligne 18 revendications 1,6 ---	1,2,7-9, 14-25
X	"MIXTURES OF FUNGICIDES, INSECTICIDES AND HERBICIDES", RESEARCH DISCLOSURE, NR. 388, PAGE(S) 489/490 XP000635427 ISSN: 0374-4353 * voir le document entier* -----	1-3,7-9, 14-25

RAPPORT DE RECHERCHE INTERNATIONALE

Renseignements relatifs aux membres des familles de brevets

De l'Organisation internationale No

PCT/FR 00/00339

Document brevet cité au rapport de recherche		Date de publication	Membre(s) de la famille de brevet(s)	Date de publication
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RAPPORT DE RECHERCHE INTERNATIONALE

Renseignements relatifs aux membres de familles de brevets

Je Internationale No

PCT/FR 00/00339

Document brevet cité au rapport de recherche	Date de publication	Membre(s) de la famille de brevet(s)	Date de publication
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PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

[stamp]

To:

BRACHOTTE Charles
AVENTIS CROPSOENCE S.A.
BP 9163
69263 LYON CEDEX 09
FRANCE

PCT

NOTIFICATION OF TRANSMITTAL OF INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Rule 71.1)

Date of mailing (day/month/year)
10.05.2001

Applicant's or agent's file reference
PH 99006

IMPORTANT NOTIFICATION

International application No.
PCT/FR00/00339

International filing date (day/month/year)
11/02/2000

Priority date (day/month/year)
12/02/1999

Applicant
AVENTIS CROPSOENCE S.A. et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.
4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the International preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/



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2091

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or Agent's file reference PH 99006	FOR FURTHER ACTION		See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/FR00/00339	International filing date (day/month/year) 11/02/2000	Priority date (day/month/year) 12/02/1999	
International Patent Classification (IPC) or national classification and IPC A01N43/50			
Applicant AVENTIS CROPS SCIENCE S.A. et al.			

1.	This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2.	<p>This REPORT consists of a total of 11 sheets including this title page.</p> <p><input type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Instruction 607 of Administrative Instructions of the PCT).</p> <p>These annexes consist of a total of sheets.</p>
3.	<p>This report contains indications relating to the following items:</p> <ul style="list-style-type: none"> I <input checked="" type="checkbox"/> Basis of the report II <input type="checkbox"/> Priority III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability IV <input type="checkbox"/> Lack of unity of invention V <input checked="" type="checkbox"/> Reasoned statement according to Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement VI <input type="checkbox"/> Certain documents cited VII <input checked="" type="checkbox"/> Certain defects in the international application VIII <input checked="" type="checkbox"/> Certain observations on the international application

Date of submission of the demand 04/09/2000	Date of completion of this report 10.05.2001
Name and mailing address of the IPEA/ <div style="display: flex; align-items: center;"> <div> European Patent Office D-80298 Munich Tel. +49 89 2399-0, Tx: 523656 epmu d Fax: +49 89 2399-4465 </div> </div>	Authorized officer: <div style="display: flex; align-items: center; justify-content: space-between;"> <div> Krattinger, B Telephone No. +49 89 2399 8550 </div> </div>

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/FR00/00339

I. Basis of the report

1. This report has been drawn up on the basis of the following elements *(the replacement sheets received by the receiving office in response to an invitation according to Article 14 are considered in the present report as "originally filed" and are not annexed to the report as they contain no amendments (Rules 70.16 and 70.17).):*

Description, pages:

1-13 as originally filed

Claims, No.:

1-25 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language which is:

- ☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of the translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. ☐ The amendments have resulted in the cancellation of:

- ☐ the description, pages
- ☐ the claims, Nos.
- ☐ the drawings, sheets/fig

5. ☐ This report has been written disregarding (some of) the amendments, which were considered as going beyond the description of the invention, as filed, as is indicated below (Rule 70.2(c)):

(All replacement sheets comprising amendments of this nature should be indicated in point 1 and attached to this report).

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/FR00/00339

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty	Yes:	Claims	6, 12-13
	No:	Claims	1-5, 7-11, 14-25
Inventive Step	Yes:	Claims	
	No:	Claims	1-25
Industrial Applicability	Yes:	Claims	1-25
	No:	Claims	

2. Citations and explanations
see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

VIII. Certain observations in the international application

The following observations on the clarity of the claims, descriptions, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

As regards point V

Reference is made to the following documents:

- D1: WO 96 03044 A
- D2: EP-A-0 531 837
- D3: FR-A-2 754 424
- D4: EP-A-0 524 496
- D5: WO 93 22921 A
- D6: WO 98 33381 A
- D7: Research disclosure No. 388, pages 489/490.
- D8: WO90/12791

Document D8 is cited in document D7. A copy of this document is attached to the present letter.

A. The present application relates to fungicide compositions which contain at least one fungicide compound inhibiting mitochondrial respiration (a) and at least one compound inhibiting sterol biosynthesis (b) (claims 1-19), methods for treating fruits with these compositions (claims 20-24) and the fruits treated with these compositions (claim 25).

Novelty

B.1. In claim 1, the expression "useful for controlling ... fruits" is not considered as describing a technical characteristic and is not taken into account for determining novelty. Furthermore, the compositions are defined by their content, not by their use. The result is that the subject-matter of claims 14-16 is strictly the same as that of claim 1, and that these claims ought to be written as claims for using the composition and not as claims for compositions (Art. 6 PCT).

2. Moreover, in claims 7, 8, 12, 14, the expressions "preferably", "for example" do not have a limiting effect on the scope of the claims. Thus, the characteristic which follows such an expression is

considered as being optional. Such expressions ought to be avoided (Art. 6 PCT).

C.1. Document D1 describes compositions comprising a compound inhibiting mitochondrial respiration of the 2-imidazolin-5-one type (= formula (I)), in particular fenamidone, and a fungicide compound inhibiting sterol biosynthesis, of the triazole, morpholine or pyrimidine type (claims 1-4, 10, examples 6, 9, 19, 21-26, 28, 29).

These compositions may contain other fungicide compounds; they comprise, in addition, solid or liquid carriers, surfactants, colloids and the like (page 8, lines 9-22), contain 0.5 to 95% by weight of active products which are in proportions of 0.001 to 2 (page 5, line 10, page 8, lines 25-26, page 9, lines 14-15); they are provided in solid or liquid form (page 9, lines 18-19).

They are applied to fruits - tomatoes, Curcubitaceae, cucumbers, cereals, wheat (page 15, line 15 to page 16, line 8) -, curatively or preventively (page 15, lines 8-9). They may be coupled with other fungicide treatments (page 2, line 9 to page 3, line 11 "at least one fungicide compound B").

These compositions are applied by spraying or daubing (page 8, line 15; page 16, lines 13-14).

Thus, in the light of the content of D1, the subject-matter of claims 1-2, 4, 7-9, 14-21, 23-25 is not novel.

The compositions of D1 do not comprise imazalil or famoxadone, and are not used for treating fruits after harvest. D1 does not specifically describe compositions comprising a compound (a), a compound (b)

and a phosphorous acid derivative (such compositions would be the result of a selection).

2. Document D2 describes the combination of a derivative inhibiting mitochondrial respiration, methyl (α -methoxyimino-2-((2-methylphenoxy)methyl))benzene acetate (=kremoxy-methyl), with other derivatives inhibiting sterol biosynthesis, such as triazoles and imizalil (page 3, lines 1-35).

These compositions may, in addition, comprise other fungicide compounds (page 4, lines 49-51), are provided in solid or liquid form (page 4, lines 52-54), comprise solid or liquid carriers, surfactants and the like (page 5, lines 3-29), contain between 0.1 and 95% by weight of active agent in (a)/(b) ratios varying from 1:10 to 10:1 (see in particular the example).

The compositions are applied to fruits - tomatoes, apples, Curcubitaceae, cucumber, wheat, barley and the like (page 5, line 33 to page 6, line 3), by spraying (page 4, line 55), curatively or preventively (page 5, line 40) and may be combined with other insecticide or fungicide treatments (page 4, lines 49-51). They may in particular be used on seeds, that is to say on seed grains (= fruits after harvest) (page 5, line 37).

Thus, the content of document D2 affects the novelty of claims 1, 2, 5, 7-9, 14-25.

The compositions of D2 do not contain famoxadone or fenamidone or a phosphorous acid derivative.

3. Document D3 describes compositions containing a compound inhibiting mitochondrial respiration similar to strobilurin, in particular azoxystrobin, and a derivative inhibiting sterol biosynthesis, namely a

compound of the triazole type (page 1, line 27 to page 2, line 26). These compositions are provided in solid or liquid form (page 5, lines 15-16), contain solid or liquid carriers, surfactants, colloids and the like (page 4, lines 6-10, 16-21), contain 0.05 to 95% of active products by weight (page 4, lines 22-25) in ratios of between 0.01 and 30.

These compositions are used curatively or preventively (page 1, line 6), are applied by dusting, film-coating or coating (page 4, line 12; page 5, line 17, 23, page 10, line 15), are used for treating seeds (= seed grains = fruits after harvest) (page 4, lines 11; page 6, lines 33-34; page 10, lines 7-15). The application may be carried out simultaneously, sequentially or separately.

Thus in the light of the content of D3, the subject-matter of claims 1, 2, 7, 8, 14-23 and 25 is not novel.

The compositions of D3 do not contain famoxadone or fenamidone or imazalil or a phosphorous acid derivative, or additional fungicide compounds and are not coupled with other treatments.

4. Document D4 describes compositions comprising kremoxy-methyl, an inhibitor of mitochondrial respiration, with derivatives of morpholine, an inhibitor of sterol biosynthesis (page 1).

These compositions may contain other fungicide or insecticide derivatives (page 3, lines 36-38), are provided in solid or liquid form (page 3, line 40), and contain solid or liquid carriers, surfactants and the like (page 3, lines 47-56).

These compositions are sprayed (page 3, lines 39-40), applied to seeds (page 3, line 45; page 4, line

24), fruits (page 4, lines 19-46), inter alia, Curcubitaceae, cucumbers, tomatoes, apples, cereals; they contain quantities identical to those of the present claims 7, 8 and 18 (page 2, lines 53, 54 and page 4, line 55, example).

Consequently, in the light of the content of D4, the subject-matter of claims 1, 2, 7, 8, 9, 14-25 is not novel.

The compositions of D3 do not contain famoxadone or fenamidone or imazalil or a phosphorous acid derivative.

5. Document D5 describes compositions comprising a compound inhibiting mitochondrial respiration which is similar to strobilurin, azoxystrobin and a derivative inhibiting sterol biosynthesis of the triazole type (claim 1). The compositions comprise 0.0001 to 95% of active substances by weight, in proportions ranging from 400:1 to 10:90 (page 1, lines 31-33; page 4, lines 28-30, page 4, lines 35-38), exist in solid or liquid form, and contain solid or liquid carriers, surfactants and the like (page 5, line 17 to page 7, line 29). These compositions may, in addition, comprise other fungicides or insecticides (page 8, lines 5-8). Some fungicides (page 8, line 9 to page 9, line 26) are inhibitors of sterol biosynthesis, such as triazoles (bromuconazole, difenoconazole and the like), imidazoles (imazalil), derivatives of morpholines (aldimorph, dodemorph and the like), of pyridines (buthiobate, pyrefenox), of pyrimidines (fenarimol, nuarimol and the like), of piperidines (fenpropidin). Others are of the phosphorous acid family (phosphorous acid, iprobenphos, pyrazophos, tolcifos-methyl, ampropyphos, edifenphos and phosetyl-Al (= fosetyl-Al)).

These compositions are used - by spraying or coating (page 5, line 3, 25) on fruits - apples, pears,

cereals, Curcubitaceae, grapes, bananas, strawberries, tomatoes, melon, lemon and the like (page 2, line 16 to page 4, line 22) - in particular after harvesting for example for oranges (page 3, line 35), seeds (page 4, lines 25-26), curatively and preventively (page 5, lines 13-14).

Consequently, in the light of the content of D5, the subject-matter of claims 1, 2, 5, 7-11, 14-25 is not novel.

The compositions of D5 do not contain famoxadone or fenamidone. D5 does not specify the quantity of additional fungicide.

6. Document D6 describes compositions based on quinazolinone and derivatives inhibiting sterol biosynthesis, including imazalil (see list pages 18, 19) or compounds inhibiting mitochondrial respiration including azoxystrobin, kremoxym-methyl and another strobilurin derivative. They are provided in liquid or solid form, contain liquid or solid carriers, surfactants and the like (page 4, lines 13-22; page 18, lines 3-7; pages 30-31). They may contain other insecticides and fungicides (page 33), including phosphorous acid derivatives, such as edifenphos, iprobenphos and fosetyl-aluminium (page 33, line 26 to 35). The percentage of active ingredient varies from 0.01 to 99% (page 30), and the proportion of compounds (a)/(b) varies from 1:30 to 30:1 (page 4, line 22-27).

These compositions are applied to fruits, seeds (page 4, line 12; page 32, lines 29, 33), curatively and preventively (page 34, lines 7-11).

If the quinazolinones of D6 have an inhibitory action on mitochondrial respiration or sterol biosynthesis, then in the light of the content of D6, the subject-matter of claims 1, 2, 5, 7-11, 14-25 is

not novel. The Applicant is invited to specify the mode of action of the quinazolinones.

Document D6 does not disclose a composition based on famoxadone, on fenamidone and does not specify the quantity of additional fungicide agent.

7. Document D7 describes compositions comprising famoxadone and other fungicide compounds inhibiting sterol biosynthesis, such as triazoles (bromuconazole, cyproconazole, imidazoles (imazalil, prochloraz and the like), pyrimidines (fenarimol, nuarimol and the like), pyridines (pyrefenox), morpholines (dodemorph, fenpropimorph and the like), piperidines (fenpropidin), thus affecting the novelty of the subject-matter of claims 1-3. These compositions are provided in solid or liquid form and optionally contain surfactants (lines 1-10).

Thus, in the light of the content of D7, the subject-matter of claims 1-3, 5, 14-17, 19 is not novel.

Document D7 does not describe the proportions and the quantities of active products, does not specify the methods of application or the subjects targeted by the application. Furthermore, it does not describe a composition specifically comprising in addition to compounds (a) and (b) a third compound (such compositions would be the result of a selection). In addition, the document does not describe compositions comprising fenamidone.

8. Document D8 describes compositions comprising famoxadone and other fungicide compounds inhibiting sterol biosynthesis (pages 8-9, 46), such as triazoles (bromuconazole, tebuconazole and the like), morpholines (fenpropimorph, page 81, line 17-19 and the like), piperidines (fenpropidin), thus affecting the novelty

of the subject-matter of claims 1-3 (page 79-81). These compositions are provided in solid or liquid form and optionally contain surfactants (page 75), contain 1 to 99% of active substance. They are used on the seeds and the fruits curatively or preventively (page 79, page 83, lines 32-38), and are applied by spraying (page 75).

Thus, in the light of the content of D8, the subject-matter of claims 1-3, 14-21, 23-25 is not novel.

Document D8 does not describe a composition specifically comprising, in addition to compounds (a) and (b), a third compound (such compositions would be the result of a selection). In addition, the document does not describe compositions comprising fenamidone or imazalil.

9. In claim 25, the fruits treated with the compositions of the inventions are not different from the point of view of their structures from the untreated fruits or from the fruits treated with other plant-protection compositions, in particular fungicides. Consequently, the subject-matter of claim 25 is not novel (Art. 33(2) PCT).

10. Consequence

In the light of the preceding text, the subject-matter of claims 1-5, 7-11, 14-25 is not novel, while the subject-matter of claims 6, 12 and 13 is novel (Art. 33(2) PCT).

D. Inventive step

Documents D1-D8 which are all considered as the closest prior art all describe compositions comprising (a) at least one fungicide compound inhibiting

mitochondrial respiration and at least one compound inhibiting sterol biosynthesis (see objections of novelty). Furthermore, these documents demonstrate the synergistic effect obtained or the efficacy of these compositions in the case of controlling fungi, in particular fungi which affect fruits (D1: page 4, lines 17-25, examples; D2: page 4, lines 21-23, example; D3: page 1, lines 12-28; examples; D4: examples; D5: page 1, line 15, example; D6: examples; D7: line 13).

Consequently, the subject-matter now claimed being identical to the disclosures of the prior art documents, the advantages of the compositions being already known, the subject-matter of the present application does not involve an inventive step (Art. 33(3)PCT).

The subject-matter of the claims ought to be restricted to preferred forms of the invention which are novel and inventive in relation to the disclosures of the prior art. Demonstration by submissions or evidence that the subject-matter of the future application involves an inventive step in relation to the prior art compositions would be necessary.

As regards point VII

Contrary to what is required by rule 5.1 a) ii) PCT, the description does not indicate the relevant prior state of the art disclosed in documents D1-D7 and does not cite these documents.

As regards point VIII

1. A discrepancy appears between the subject-matter of claim 2 and its basis in the description: the description defines as a compound inhibiting mitochondrial respiration "strobilurin and analogous compounds or derivatives" whereas the claim only

defines a few specific analogues, thus making the subject-matter of the claim obscure (page 3, line 9) (Art. 6 PCT).

Furthermore, the expression "strobilurin and analogous compounds or derivatives" is vague since it does not make it possible to precisely define, in terms of structures, the compounds included under this term, thus making the description vague and therefore the subject-matter of the claim obscure (Art. 6 PCT).

An additional discrepancy appears between the subject-matter of claim 2 and its basis in the description: the description defines as a compound inhibiting mitochondrial respiration "discostrobin" (page 3, line 11) whereas the claim defines "discoxystrobin", thus making the subject-matter of the claim obscure (page 3, line 9). IPEA has not found the chemical formula for this compound. The Applicant is invited to specify it.

2. A discrepancy appears between the subject-matter of claim 9 and its basis in the description on page 4, paragraph 33. The description defines fungicides suitable for treatments of fungal diseases of fruits, whereas the claim does not contain this characteristic, thus making the subject-matter of the claim obscure (Art. 6 PCT).

3. The subject-matter of claim 23 is inconsistent with the subject-matter of claims 1-19 and 20. The subject-matter of claims 1-19 consists of a composition comprising one or more compounds (a), one or more compounds (b) and optionally a third type of fungicide. If these various compounds are applied sequentially or separately, they cannot form part of the same composition and this manner of applying the products does not therefore form part of the invention as defined in claims 1-22, 24 and 25, thus making the

scope of the set of claims obscure (Art. 6 PCT). The products (a), (b) and the optional other fungicides should form part of one and the same composition and can only be applied simultaneously in the context of the present invention.

TRAITE DE COOPERATION EN MATIERE DE BREVETS

PCT

REC'D 15 MAY 2001

WIPO PCT

RAPPORT D'EXAMEN PRELIMINAIRE INTERNATIONAL



(article 36 et règle 70 du PCT)

Référence du dossier du déposant ou du mandataire PH 99006	POUR SUITE A DONNER voir la notification de transmission du rapport d'examen préliminaire international (formulaire PCT/IPEA/416)	
Demande internationale n° PCT/FR00/00339	Date du dépôt international (jour/mois/année) 11/02/2000	Date de priorité (jour/mois/année) 12/02/1999
Classification internationale des brevets (CIB) ou à la fois classification nationale et CIB A01N43/50		
Déposant AVENTIS CROPS SCIENCE S.A. et al.		

- Le présent rapport d'examen préliminaire international, établi par l'administration chargée de l'examen préliminaire international, est transmis au déposant conformément à l'article 36.
- Ce RAPPORT comprend 11 feuilles, y compris la présente feuille de couverture.
 - ☐ Il est accompagné d'ANNEXES, c'est-à-dire de feuilles de la description, des revendications ou des dessins qui ont été modifiées et qui servent de base au présent rapport ou de feuilles contenant des rectifications faites auprès de l'administration chargée de l'examen préliminaire international (voir la règle 70.16 et l'instruction 607 des Instructions administratives du PCT).

Ces annexes comprennent feuilles.

- Le présent rapport contient des indications relatives aux points suivants:
 - I ☒ Base du rapport
 - II ☐ Priorité
 - III ☐ Absence de formulation d'opinion quant à la nouveauté, l'activité inventive et la possibilité d'application industrielle
 - IV ☐ Absence d'unité de l'invention
 - V ☒ Déclaration motivée selon l'article 35(2) quant à la nouveauté, l'activité inventive et la possibilité d'application industrielle; citations et explications à l'appui de cette déclaration
 - VI ☐ Certains documents cités
 - VII ☒ Irrégularités dans la demande internationale
 - VIII ☒ Observations relatives à la demande internationale

Date de présentation de la demande d'examen préliminaire internationale 04/09/2000	Date d'achèvement du présent rapport 10.05.2001
Nom et adresse postale de l'administration chargée de l'examen préliminaire international:  Office européen des brevets D-80298 Munich Tél. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Fonctionnaire autorisé Krattinger, B N° de téléphone +49 89 2399 8550 

RAPPORT D'EXAMEN PRÉLIMINAIRE INTERNATIONAL

Demande internationale n° PCT/FR00/00339

I. Bas du rapport

1. En ce qui concerne les **éléments** de la demande internationale (*les feuilles de remplacement qui ont été remises à l'office récepteur en réponse à une invitation faite conformément à l'article 14 sont considérées dans le présent rapport comme "initialement déposées" et ne sont pas jointes en annexe au rapport puisqu'elles ne contiennent pas de modifications (règles 70.16 et 70.17)*):

Description, pages:

1-13 version initiale

Revendications, N°:

1-25 version initiale

2. En ce qui concerne la **langue**, tous les éléments indiqués ci-dessus étaient à la disposition de l'administration ou lui ont été remis dans la langue dans laquelle la demande internationale a été déposée, sauf indication contraire donnée sous ce point.

Ces éléments étaient à la disposition de l'administration ou lui ont été remis dans la langue suivante: , qui est :

- ☐ la langue d'une traduction remise aux fins de la recherche internationale (selon la règle 23.1(b)).
- ☐ la langue de publication de la demande internationale (selon la règle 48.3(b)).
- ☐ la langue de la traduction remise aux fins de l'examen préliminaire internationale (selon la règle 55.2 ou 55.3).

3. En ce qui concerne les **séquences de nucléotides ou d'acide aminés** divulguées dans la demande internationale (le cas échéant), l'examen préliminaire internationale a été effectué sur la base du listage des séquences :

- ☐ contenu dans la demande internationale, sous forme écrite.
- ☐ déposé avec la demande internationale, sous forme déchiffrable par ordinateur.
- ☐ remis ultérieurement à l'administration, sous forme écrite.
- ☐ remis ultérieurement à l'administration, sous forme déchiffrable par ordinateur.
- ☐ La déclaration, selon laquelle le listage des séquences par écrit et fourni ultérieurement ne va pas au-delà de la divulgation faite dans la demande telle que déposée, a été fournie.
- ☐ La déclaration, selon laquelle les informations enregistrées sous déchiffrable par ordinateur sont identiques à celles du listage des séquences Présenté par écrit, a été fournie.

4. Les modifications ont entraîné l'annulation :

- ☐ de la description, pages :
- ☐ des revendications, n°s :
- ☐ des dessins, feuilles :



**RAPPORT D'EXAMEN
PRÉLIMINAIRE INTERNATIONAL**

Demande internationale n° PCT/FR00/00339

5. ☐ Le présent rapport a été formulé abstraction faite (de certaines) des modifications, qui ont été considérées comme allant au-delà de l'exposé de l'invention tel qu'il a été déposé, comme il est indiqué ci-après (règle 70.2(c)) :

(Toute feuille de remplacement comportant des modifications de cette nature doit être indiquée au point 1 et annexée au présent rapport)

6. Observations complémentaires, le cas échéant :

V. Déclaration motivée selon l'article 35(2) quant à la nouveauté, l'activité inventive et la possibilité d'application industrielle; citations et explications à l'appui de cette déclaration

1. Déclaration

Nouveauté	Oui : Revendications 6, 12-13
	Non : Revendications 1-5, 7-11, 14-25
Activité inventive	Oui : Revendications
	Non : Revendications 1-25
Possibilité d'application industrielle	Oui : Revendications 1-25
	Non : Revendications

2. Citations et explications
voir feuille séparée

VII. Irrégularités dans la demande internationale

Les irrégularités suivantes, concernant la forme ou le contenu de la demande internationale, ont été constatées :
voir feuille séparée

VIII. Observations relatives à la demande internationale

Les observations suivantes sont faites au sujet de la clarté des revendications, de la description et des dessins et de la question de savoir si les revendications se fondent entièrement sur la description :
voir feuille séparée

Concernant le point V

Il est fait référence aux documents suivants:

- D1: WO 96 03044 A
- D2: EP-A-0 531 837
- D3: FR-A-2 754 424
- D4: EP-A-0 524 496
- D5: WO 93 22921 A
- D6: WO 98 33381 A
- D7: Research disclosure, nr. 388, pages 489/490.
- D8: WO90/12791

Le document D8 est cité dans le document D7. Une copie de ce document est jointe à la présente lettre.

A. La présente demande concerne des compositions fongicides qui contiennent au moins un composé fongicide inhibiteur de la respiration mitochondriale (a) et au moins un composé inhibiteur de la biosynthèse de stérols (b) (revendications 1-19), des procédés de traitement des fruits avec ces compositions (revendications 20-24) et les fruits traités par ces compositions (revendications 25).

Nouveauté

B.1. Dans la revendications 1, l'expression "utiles pour lutter...fruits" n'est pas considérée comme décrivant une caractéristique technique et n'est pas prise en compte pour juger de la nouveauté. De plus, les compositions sont définies par leur contenu, non par leur utilisation. Il en résulte que l'objet des revendications 14-16 est strictement le même que celui de la revendication 1, et que ces revendications devraient être rédigées comme des revendications d'utilisation de la composition et non comme des revendications de compositions (Art. 6 PCT).

2. Par ailleurs, dans les revendications 7, 8, 12, 14, les expressions "de préférence", "par exemple" n'ont pas d'effet limitatif sur la portée des revendications. Ainsi la caractéristique qui suit une telle expression est considérée comme facultative. De telles expressions devraient être évitées (Art. 6 PCT).

C.1. Le document D1 décrit des compositions comprenant un composé inhibiteur de la respiration mitochondriale de type 2-imidazoline-5-one (= formule (I)), en particulier la fénamidone, et un composé fongicide inhibiteur de la biosynthèse des stérols, du type triazole, morpholine, pyrimidine (revendications 1-4, 10, exemples 6, 9, 19, 21-26, 28, 29).

Ces compositions peuvent contenir d'autres composés fongicides; elles comprennent en outre des supports solides ou liquides, des tensioactifs, des colloïdes, etc. (page 8, lignes 9-22), contiennent 0.5 à 95% en poids de produits actifs qui sont dans des proportions 0.001 à 2 (page 5, lignes 10; page 8, lignes 25-26, page 9, lignes 14-15); elles se présentent sous forme solide ou liquide (page 9, lignes 18-19).

Elles sont appliquées sur des fruits - les tomates, cucurbitacées, concombres, céréales, blé (page 15, ligne 15 à page 16, lignes 8)-, à titre curatif ou préventif (page 15, lignes 8-9). Elles peuvent être couplées à d'autres traitements fongicides (page 2, ligne 9 à page 3, ligne 11 "au moins un composé fongicide B")

Ces compositions sont appliquées par pulvérisation ou badigeonnage (page 8, ligne 15; page 16, lignes 13-14).

Ainsi, au vu du contenu de D1, l'objet des revendications 1-2, 4, 7-9, 14-21, 23-25 n'est pas nouveau.

Les compositions de D1 ne comprennent pas d'imazalil ou de famoxadone, et ne sont pas utilisées pour traiter les fruits après récolte. D1 ne décrit pas spécifiquement de compositions comprenant un composé (a), un composé (b) et un dérivé d'acide phosphoreux (de telles compositions seraient le résultat d'une sélection).

2. Le document D2 décrit l'association d'un dérivé inhibiteur de la respiration mitochondriale, le méthyl (α -methoxyimino-2-((2-méthylphénoxy)méthyl))benzène acetate (= krémoxyméthyl), avec d'autres dérivés inhibiteurs de la biosynthèse des stérols, tels les triazoles et l'imizalil (page 3, lignes 1-35).

Ces compositions peuvent en outre comprendre d'autres composés fongicides (page 4, lignes 49-51), se présentent sous forme solide ou liquide (page 4, lignes 52-54), comprennent des supports solides ou liquides, des agents tensioactifs, etc. (page 5, lignes 3-29), contiennent entre 0,1 et 95% en poids d'agent actif dans des proportions (a)/(b) variant de 1:10 à 10:1 (voir notamment l'exemple).

Les compositions sont appliquées sur des fruits -tomates, pommes,

curcubitacées, concombre, blé, orge, etc. ((page 5, ligne 33 à page 6, ligne 3), par pulvérisation (page 4, ligne 55), à titre curatif ou préventif (page 5, ligne 40) et peuvent être combinées avec d'autres traitements insecticides ou fongicides (page 4, lignes 49-51). Elles peuvent être notamment utilisées sur les semences, c'est à dire sur les graines (= fruits après récolte) (page 5, lignes 37)

Ainsi le contenu du document D2 affecte la nouveauté des revendications 1, 2, 5, 7-9, 14-25.

Les compositions de D2 ne contiennent pas de famoxadone, ni de fénamidone, ni de dérivé de l'acide phosphoreux.

3. Le document D3 décrit des compositions contenant un composé inhibiteur de la respiration mitochondriale analogue de la strobilurine, en particulier l'azoxystrobine, et un dérivé inhibiteur de la biosynthèse des stérols, à savoir un composé de type triazole (page 1, lignes 27 à page 2, ligne 26). Ces compositions se présentent sous forme solide ou liquide (page 5, lignes 15-16), contiennent des supports solides ou liquides, des tensio-actifs, des colloïdes... (page 4, lignes 6-10, 16-21), contiennent 0.05 à 95% de produits actifs en poids (page 4, lignes 22-25) dans des rapport compris entre 0.01 et 30.

Ces compositions sont utilisées à titre curatif ou préventif (page 1, ligne 6), sont appliquées par poudrage, pelliculage ou enrobage (page 4, ligne 12; page 5, ligne 17, 23, page 10, ligne 15), sont utilisées pour traiter les semences (= graines = fruits après récoltes) (page 4, lignes 11; page 6, lignes 33-34; page 10, lignes 7-15). L'application peut être simultanée, séquentielle ou séparée.

Ainsi au vu du contenu de D3, l'objet des revendications 1, 2, 7, 8, 14-23 et 25 n'est pas nouveau.

Les compositions de D3 ne contiennent ni famoxadone, ni fénamidone, ni imazalil, ni dérivé d'acide phosphoreux, ni de composés fongicides supplémentaires et ne sont pas couplées à d'autres traitements.

4. Le document D4 décrit des compositions comprenant le krémoxyméthyl, inhibiteur de la respiration mitochondriale, avec des dérivés de la morpholine, inhibiteur de la biosynthèse des stérols (page 1).

Ces compositions peuvent contenir d'autres dérivés fongicides ou insecticides

(page 3, lignes 36-38), se présentent sous forme solide, liquide (page 3, ligne 40), contiennent des supports solides, liquides, des tensio actifs, ... (page 3, lignes 47-56),

Ces compositions sont pulvérisées (page 3, lignes 39-40), appliquées à des semences (page 3, ligne 45; page 4, ligne 24), des fruits (page 4, lignes 19-46), entre autre les cucurbitacées, les concombres, les tomates, les pommes, les céréales; elles contiennent des quantités identiques à celles des présentes revendications 7, 8 et 18 (page 2, lignes 53, 54 et page 4, ligne 55, exemple).

Par conséquent, au vu du contenu de D4, l'objet des revendications 1, 2, 7, 8, 9, 14-25 n'est pas nouveau.

Les compositions de D3 ne contiennent ni famoxadone, ni fénamidone, ni imazalil, ni dérivé d'acide phosphoreux.

5. Le document D5 décrit des compositions comprenant un composé inhibiteur de la respiration mitochondriale analogue de la strobilurine, l'azoxystrobine et un dérivé inhibiteur de la biosynthèse des stérols de type triazole (revendication 1). Les compositions comprennent 0.0001 à 95% de matières actives en poids, dans des proportions variant de 400:1 à 10:90 (page 1, lignes 31-33; page 4, lignes 28-30, page 4, lignes 35-38), se présentent sous forme solide, liquide, contiennent des supports solides, liquides, des tensioactifs... (page 5, ligne 17 à page 7, ligne 29). Ces compositions peuvent en outre comporter d'autres fongicides ou insecticides (page 8, lignes 5-8). Certains des fongicides (page 8, lignes 9 à page 9, lignes 26), sont des inhibiteurs de la biosynthèses des stérols, comme les triazoles (bromuconazole, difenoconazole...), les imidazoles (imazalil), les dérivés de morpholines (aldimorph, dodemorph...), de pyridines (buthiobate, pyrefenox), de pyrimidines (fenarimol, nuarimol..), de pipéridines (fenpropidin). D'autres sont de la famille de l'acide phosphoreux (phosphorus acid, iprobenphos, pyrazophos, tolclfos-methyl, ampropypphos, edifenphos et phoselyl-Al (= fosetyl-Al).

Ces compositions sont utilisées - par pulvérisation ou enrobage (page 5, ligne 3, 25) sur des fruits - pommes, poires, céréales, cucurbitacées, raisins, bananes, fraises, tomates, melon, citron etc. (page 2, ligne 16 à page 4, ligne 22)- notamment après récolte par exemple pour les oranges, (page 3, lignes 35), les graines (page 4, lignes 25-26), à titre curatif et préventif (page 5, lignes 13-14).

Par conséquent, au vu du contenu de D5, l'objet des revendications 1, 2, 5, 7-11,

14-25 n'est pas nouveau.

Les compositions de D5 ne contiennent ni famoxadone, ni fénamidone. D5 ne précise pas la quantité de fongicide supplémentaire.

6. Le document D6 décrit des compositions à base de quinazolinone et de dérivés inhibiteur de la biosynthèse des stérols, dont l'imazalil (voir liste pages 18, 19) ou de composés inhibiteurs de la respiration mitochondriale dont l'azoxystrobine, le krémoxym-méthyl et un autre dérivé de la strobilurine. Elles se présentent sous forme liquide ou solide, contiennent des supports liquides, solides, des tensioactifs, etc. (page 4, lignes 13-22; page 18, lignes 3-7; pages 30-31). Ils peuvent contenir d'autres insecticides et fongicides (page 33), dont des dérivés d'acide phosphoreux, comme edifenphos, iprobenphos et le fosétyl-aluminium (page 33, ligne 26 à 35). Le pourcentage d'ingrédient actif varie de 0.01 à 99% (page 30), et la proportion des composés (a)/(b) varie de 1:30 à 30:1 (page 4, ligne 22-27).

Ces compositions sont appliquées sur les fruits, les graines (page 4, ligne 12; page 32, lignes 29, 33), à titre curatif et préventif (page 34, lignes 7-11)

Si les quinazolinone de D6 ont une action inhibitrice de la respiration mitochondriale ou de la biosynthèse des stérols, alors au vu du contenu de D6, l'objet des revendications 1, 2, 5, 7-11, 14-25 n'est pas nouveau. Le Demandeur est invité à préciser le mode d'action des quinazolinones.

Le document D6 ne divulgue pas de composition à base de famoxadone, de fénamidone et ne précise pas la quantité de l'agent fongicide supplémentaire.

7. Le document D7 décrit des compositions comprenant la famoxadone et d'autres composés fongicides inhibiteurs de la biosynthèse des stérols, tels les triazoles (bromuconazole, cyproconazole, les imidazoles (imazalil, prochloraz..), les pyrimidines (fenarimol, nuarimol..), les pyridines (pyrefenox), les morpholines (dodemorph, fenpropimorph...), les pipéridines (fenpropidin), affectant ainsi la nouveauté de l'objet des revendications 1-3. Ces compositions se présentent sous forme solide, liquide et contiennent éventuellement des tensio-actif (lignes 1-10)

Ainsi, au vu du contenu de D7, l'objet des revendications 1-3, 5, 14-17, 19 n'est pas nouveau.

Le document D7 ne décrit pas les proportions et les quantités de produits actifs, ne précisent pas les procédés d'application, ni les objets visés par l'application. De plus il ne décrit pas de composition comprenant spécifiquement en plus des composés (a) et (b) un troisième composé (de telles compositions seraient le résultat d'une sélection). En outre le document ne décrit pas de compositions comprenant de fénamidone.

8. Le document D8 décrit des compositions comprenant la famoxadone et d'autres composés fongicides inhibiteurs de la biosynthèse des stérols (pages 8-9, 46), tels les triazoles (bromuconazole, tebuconazole...), les morpholines (fenpropimorph, page 81, ligne 17-19...), les pipéridines (fenpropidin), affectant ainsi la nouveauté de l'objet des revendications 1-3 (page 79-81). Ces compositions se présentent sous forme solide, liquide et contiennent éventuellement des tensio-actifs (page 75), contiennent 1 à 99% de matière active. Elles sont utilisées sur les graines et les fruits à titre curatif ou préventif (page 79, page 83, lignes 32-38), et sont appliquées par pulvérisation (page 75).

Ainsi, au vu du contenu de D8, l'objet des revendications 1-3, 14-21, 23-25 n'est pas nouveau.

Le document D8 ne décrit pas de composition comprenant spécifiquement en plus des composés (a) et (b) un troisième composé (de telles compositions seraient le résultat d'une sélection). En outre le document ne décrit pas de compositions comprenant de fénamidone ou l'imazalil.

9. A la revendication 25, les fruits traités par les compositions de l'inventions ne diffèrent pas du point de vue de leur structures des fruits non traités ou des fruits traités avec d'autres compositions phytosanitaires, en particulier, fongicides. Par conséquent l'objet de la revendication 25 n'est pas nouveau (Art. 33(2) PCT).

10. Bilan

Au vu de ce qui précède l'objet des revendications 1-5, 7-11, 14-25 n'est pas nouveau, alors que l'objet des revendications 6, 12 et 13 est nouveau (Art. 33(2) PCT,

D. Activité inventive

Les documents D1-D8 qui sont tous considérés comme l'art antérieur le plus proche, décrivent tous des compositions comprenant (a) au moins un composé fongicide inhibiteur de la respiration mitochondriale et au moins un composé inhibiteur de la biosynthèse de stérols (voir objections de nouveauté). De plus ces documents démontrent l'effet synergique obtenu ou l'efficacité de ces compositions lorsqu'il s'agit de lutter contre les champignons, en particulier les champignons affectant les fruits (D1: page 4, lignes 17-25. exemples ; D2 : page 4, lignes 21-23, exemple; D3 : page 1, lignes 12-28; exemples; D4: exemples; D5 : page 1, ligne 15, exemple ; D6 : exemples; D7 : ligne 13).

Par conséquent, l'objet présentement revendiqué étant identique aux divulgations des documents de l'art antérieur, les avantages des compositions étant déjà connues, l'objet de la présente demande n'implique pas d'activité inventive (Art. 33(3) PCT).

L'objet des revendications devraient être restreint à des formes préférées de l'invention qui soient nouvelles et inventives par rapport aux révélations de l'art antérieur. La démonstration par argumentation ou évidence que l'objet de la future demande implique une activité inventive par rapport aux compositions de l'art antérieur serait nécessaire.

Concernant le point VII

Contrairement à ce qu'exige la règle 5.1 a) ii) PCT, la description n'indique pas l'état de la technique antérieure pertinent exposé dans les documents D1-D7 et ne cite pas ces documents.

Concernant le point VIII

1. Une disconcordance apparaît entre l'objet de la revendication 2 et son fondement dans la description : la description définit comme composé inhibiteur de la respiration mitochondriale "la strobilurine et dérivés ou composés analogues" alors que la revendications ne définit que quelques analogues précis, rendant ainsi l'objet de la revendication obscure (page 3, ligne 9) (Art. 6 PCT).

De plus l'expression "la strobilurine et dérivés ou composés analogues" est vague

puisqu'elle ne permet pas de définir précisément en terme de structures les composés compris sous ce terme, rendant ainsi la description vague et donc l'objet de la revendication obscure (Art. 6 PCT).

Une disconcordance supplémentaire apparaît entre l'objet de la revendication 2 et son fondement dans la description : la description définit comme composé inhibiteur de la respiration mitochondriale "la discostrobine" (page 3, ligne 11) alors que la revendication définit la "discoxystrobine", rendant ainsi l'objet de la revendication obscure (page 3, ligne 9). L'IPEA n'a pas trouvée quelle était la formule chimique de ce composé. Le Demandeur est invité à la préciser.

2. Une disconcordance apparaît entre l'objet de la revendication 9 et son fondement dans la description à la page 4, paragraphe 33. La description définit des fongicides adaptés aux traitements des maladies fongicides du fruits, alors que la revendication ne contient pas cette caractéristique, rendant ainsi l'objet de la revendication obscure (Art. 6 PCT).

3. L'objet de la revendication 23 est incohérent avec l'objet des revendications 1-19 et 20. L'objet des revendications 1-19 consiste en une composition comprenant un ou des composés (a), un ou des composés (b) et éventuellement un troisième type de fongicide. Si ces différents composés sont appliqués de manière séquentiel ou séparée, ils ne peuvent faire partie de la même composition et cette manière d'appliquer les produits ne fait donc pas partie de l'invention telle que définie aux revendications 1-22, 24 et 25, rendant ainsi la portée du jeu de revendication obscure (Art. 6 PCT). Les produits (a), (b) et les éventuels autres fongicides doivent faire partie d'une seule et même composition et ne peuvent être appliqués que simultanément dans le cadre de la présente invention.

TRAITE DE COOPERATION EN MATIERE DE BREVETS

PCT

RAPPORT DE RECHERCHE INTERNATIONALE

(article 18 et règles 43 et 44 du PCT)

Référence du dossier du déposant ou du mandataire PH 99006	POUR SUITE A DONNER voir la notification de transmission du rapport de recherche international (formulaire PCT/ISA/220) et, le cas échéant, le point 5 ci-après	
Demande internationale n° PCT/FR 00/ 00339	Date du dépôt international (jour/mois/année) 11/02/2000	(Date de priorité (la plus ancienne) (jour/mois/année) 12/02/1999
Déposant AVENTIS CROPS SCIENCE S.A. et al.		

Le présent rapport de recherche internationale, établi par l'administration chargée de la recherche internationale, est transmis au déposant conformément à l'article 18. Une copie en est transmise au Bureau International.

Ce rapport de recherche internationale comprend 3 feuilles.

☒ Il est aussi accompagné d'une copie de chaque document relatif à l'état de la technique qui y est cité.

1. Base du rapport

- a. En ce qui concerne la langue, la recherche internationale a été effectuée sur la base de la demande internationale dans la langue dans laquelle elle a été déposée, sauf indication contraire donnée sous le même point.
- ☐ la recherche internationale a été effectuée sur la base d'une traduction de la demande internationale remise à l'administration.
- b. En ce qui concerne les séquences de nucléotides ou d'acides aminés divulguées dans la demande internationale (le cas échéant), la recherche internationale a été effectuée sur la base du listing des séquences :
- ☐ contenu dans la demande internationale, sous forme écrite.
- ☐ déposée avec la demande internationale, sous forme déchiffrable par ordinateur.
- ☐ remis ultérieurement à l'administration, sous forme écrite.
- ☐ remis ultérieurement à l'administration, sous forme déchiffrable par ordinateur.
- ☐ La déclaration, selon laquelle le listing des séquences présenté par écrit et fourni ultérieurement ne va pas au-delà de la divulgation faite dans la demande telle que déposée, a été fournie.
- ☐ La déclaration, selon laquelle les informations enregistrées sous forme déchiffrable par ordinateur sont identiques à celles du listing des séquences présenté par écrit, a été fournie.

2. ☐ Il a été estimé que certaines revendications ne pouvaient pas faire l'objet d'une recherche (voir le cadre I).

3. ☐ Il y a absence d'unité de l'invention (voir le cadre II).

4. En ce qui concerne le titre,

- ☒ le texte est approuvé tel qu'il a été remis par le déposant.
- ☐ Le texte a été établi par l'administration et a la teneur suivante:

5. En ce qui concerne l'abrégé,

- ☒ le texte est approuvé tel qu'il a été remis par le déposant
- ☐ le texte (reproduit dans le cadre III) a été établi par l'administration conformément à la règle 38.2b). Le déposant peut présenter des observations à l'administration dans un délai d'un mois à compter de la date d'expédition du présent rapport de recherche internationale.

6. La figure des dessins à publier avec l'abrégé est la Figure n°

- ☐ suggérée par le déposant.
- ☐ parce que le déposant n'a pas suggéré de figure.
- ☐ parce que cette figure caractérise mieux l'invention.

☐ Aucune des figures n'est à publier.

RAPPORT DE RECHERCHE INTERNATIONALE

Demande Internationale No
PCT/FR 00/00339

A. CLASSEMENT DE L'OBJET DE LA DEMANDE CIB 7 A01N43/50 A01N57/12 A01N61/00		
Selon la classification internationale des brevets (CIB) ou à la fois selon la classification nationale et la CIB		
B. DOMAINES SUR LESQUELS LA RECHERCHE A PORTE Documentation minimale consultée (système de classification suivi des symboles de classement) CIB 7 A01N		
Documentation consultée autre que la documentation minimale dans la mesure où ces documents relèvent des domaines sur lesquels a porté la recherche		
Base de données électronique consultée au cours de la recherche internationale (nom de la base de données, et si réalisable, termes de recherche utilisés)		
C. DOCUMENTS CONSIDERES COMME PERTINENTS		
Catégorie °	Identification des documents cités, avec, le cas échéant, l'indication des passages pertinents	no. des revendications visées
X	WO 96 03044 A (RHONE POULENC) 8 février 1996 (1996-02-08) page 1, ligne 31 -page 4, ligne 13 exemples 1,2,12,21-29 ---	1,2,4, 7-12, 14-25
X	EP 0 531 837 A (BASF) 17 mars 1993 (1993-03-17) * voir le document entier * ---	1,2,5,7, 8,14-25
X	FR 2 754 424 A (RHONE POULENC) 17 avril 1998 (1998-04-17) * voir le document entier* ---	1,2,7,8, 14,17-19
X	EP 0 524 496 A (BASF) 27 janvier 1993 (1993-01-27) *voir le document entier* ---	1,2,7-9, 14-25
-/-		
<div style="display: flex; justify-content: space-between;"> <input checked="" type="checkbox"/> Voir la suite du cadre C pour la fin de la liste des documents <input checked="" type="checkbox"/> Les documents de familles de brevets sont indiqués en annexe </div>		
° Catégories spéciales de documents cités:		
<div style="display: flex;"> <div style="flex: 1;"> <p>"A" document définissant l'état général de la technique, non considéré comme particulièrement pertinent</p> <p>"E" document antérieur, mais publié à la date de dépôt international ou après cette date</p> <p>"L" document pouvant jeter un doute sur une revendication de priorité ou cité pour déterminer la date de publication d'une autre citation ou pour une raison spéciale (telle qu'indiquée)</p> <p>"O" document se référant à une divulgation orale, à un usage, à une exposition ou tous autres moyens</p> <p>"P" document publié avant la date de dépôt international, mais postérieurement à la date de priorité revendiquée</p> </div> <div style="flex: 1;"> <p>"T" document ultérieur publié après la date de dépôt international ou la date de priorité et n'appartenant pas à l'état de la technique pertinent, mais cité pour comprendre le principe ou la théorie constituant la base de l'invention</p> <p>"X" document particulièrement pertinent; l'invention revendiquée ne peut être considérée comme nouvelle ou comme impliquant une activité inventive par rapport au document considéré isolément</p> <p>"Y" document particulièrement pertinent; l'invention revendiquée ne peut être considérée comme impliquant une activité inventive lorsque le document est associé à un ou plusieurs autres documents de même nature, cette combinaison étant évidente pour une personne du métier</p> <p>"&" document qui fait partie de la même famille de brevets</p> </div> </div>		
Date à laquelle la recherche internationale a été effectivement achevée	Date d'expédition du présent rapport de recherche internationale	
3 avril 2000	11/04/2000	
Nom et adresse postale de l'administration chargée de la recherche internationale		Fonctionnaire autorisé
Office Européen des Brevets, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Fort, M

C.(suite) DOCUMENTS CONSIDERES COMME PERTINENTS

Catégorie	Identification des documents cités, avec, le cas échéant, l'indication des passages pertinents	no. des revendications visées
X	WO 93 22921 A (ZENECA) 25 novembre 1993 (1993-11-25) * voir le document entier*	1,2,7-9, 14-25
X	WO 98 33381 A (DU PONT DE NEMOURS) 6 août 1998 (1998-08-06) * voir p.12, "Preferred 6"* page 18, ligne 8 -page 19, ligne 21 page 34, ligne 6 - ligne 18 revendications 1,6	1,2,7-9, 14-25
X	"MIXTURES OF FUNGICIDES, INSECTICIDES AND HERBICIDES", RESEARCH DISCLOSURE, NR. 388, PAGE(S) 489/490 XP000635427 ISSN: 0374-4353 * voir le document entier*	1-3,7-9, 14-25

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International Application No

PO 00/00339

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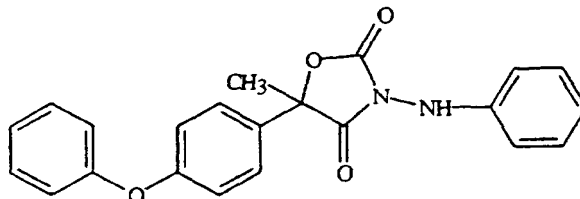
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Mixtures of Fungicides, Insecticides and Herbicides

The compound 5-methyl-5-(4-phenoxyphenyl)-3-phenylamino-2,4-oxazolidinedione which has Formula I:



I

is described in WO 90/12791 together with its preparation, use as a fungicide and fungicidal compositions containing it. Other methods for the preparation of the compound of Formula I are described in WO 94/11359.

The compound of Formula I may be used as a fungicide in its own right or it may be used as a fungicide in the form of a composition comprising a solid or liquid carrier or diluent and optionally a wetting, dispersing or emulsifying agent. It may also be used with one or more other fungicides, with one or more insecticides, and/or with one or more herbicides.

The compound of Formula I may be used in any proportion with other fungicides. By including another fungicide, the resulting composition can have a broader spectrum of activity, a greater level of intrinsic activity than the compound alone, or a greater level of activity than the additive control of the individual components of the composition. Examples of fungicidal compounds which may be included are: acypetacs, anilazine, azaconazole, azoxystrobin (ICIA5504), benalaxyl, benomyl, biphenyl, bitertanol, blasticidin-S, borax, Bordeaux mixture (tribasic copper sulfate), bromuconazole, bupirimate, butylamine, calcium polysulfide, captafol, captan, carbendazim, carboxin, chinomethionat, chloroneb, chlorothalonil, chlozolate, copper hydroxide, copper oxychloride, copper salts, copper sulfate, cuprous oxide, cymoxanil, cyproconazole, cyprodinil (CGA 219417), dazomet, debacarb, dichlofluanid, dichlone, dichlorophen, diclomezine, dicloran, diethofencarb, difenoconazole, dimethirimol, dimethomorph, diniconazole, diniconazole-M, dinocap, diphenylamine, dithianon, DNOC, dodemorph, dodine, edifenphos, epoxiconazole (BAS 480F), ethirimol, ethoxyquin, etridiazole, fenarimol, fenbuconazole, fenfuram, fenpiclonil, fenpropidin, fenpropimorph, fentin, ferbam, ferimzone, fluazinam, fludioxonil, fluoromide, fluquinconazole, flusilazole, flusulfamide, flutolanil, flutriafol, folpet, formaldehyde, fosetyl-aluminum, fuberidazole, furalaxyl, guazatine, GY-81, hexachlorobenzene, hexaconazole, 8-hydroxyquinoline sulfate, hymexazol, ICIA0858, imazalil, imibenconazole, iminoctadine, ipconazole, iprobenfos, iprodione, isopamphos, isoprothiolane, kasugamycin, kresoxim-methyl (BAS 490F), mancozeb, maneb, mepanipyrim, mepronil, mercuric chloride, mercuric oxide, mercurous chloride, metalaxyl, metam, metconazole, methasulfocarb, methyl isothiocyanate, metiram, myclobutanil, nabam, naphthenic acid, natamycin, neo-asozin (ferric methanearsonate), nickel bis(dimethyldithiocarbamate), nitrothal-isopropyl, nuarimol, octhilinone, ofurace, oxadixyl, oxine-copper, oxycarboxin,

pefurazoate, penconazole, pencycuron, pentachlorophenol, phenylmercury acetate, 2-phenylphenol, phosdiphen, phthalide, piperalin, polyoxins, probenazole, prochloraz, procymidone, propamocarb, propiconazole, propineb, pyrazophos, pyrifenox, pyrimethanil, pyroquilon, quintozone, SSF-109, sulfur, tar oils, tebuconazole, tecnazene, tetraconazole, thiabendazole, thifluzamide, thiophanate-methyl, thiram, tolclofos-methyl, tolylfluand, triadimefon, triadimenol, triazoxide, tricyclazole, tridemorph, triflumizole, triforine, triticonazole, validamycin, vinclozolin, zineb and ziram.

Suitable insecticides which may be incorporated in a composition with the compound of Formula I include: abamectin, acephate, azinphos-methyl, bifenthrin, buprofezin, carbofuran, chlorpyrifos, chlorpyrifos-methyl, cyfluthrin, beta-cyfluthrin, deltamethrin, diafenthiuron, diazinon, diflubenzuron, dimethoate, esfenvalerate, fenpropathrin, fenvalerate, fipronil, flucythrinate, tau-fluvalinate, fonophos, imidacloprid, isofenphos, malathion, metaldehyde, methamidophos, methidathion, methomyl, methoprene, methoxychlor, monocrotophos, oxamyl, parathion, parathion-methyl, permethrin, phorate, phosalone, phosmet, phosphamidon, pirimicarb, profenofos, rotenone, sulprofos, tebufenozide, tefluthrin, terbufos, tetrachlorvinphos, thiodicarb, tralomethrin, trichlorfon and triflururon.

Suitable herbicides which may be incorporated in a composition with the compound of Formula I include: acetochlor, acifluorfen and its sodium salt, aclonifen, acrolein (2-propenal), alachlor, ametryn, amidosulfuron, amitrole, ammonium sulfamate, anilofos, asulam, atrazine, azimsulfuron, benazolin, benazolin-ethyl, benfluralin, benfuresate, bensulfuron-methyl, bensulide, bentazone, bifenox, bromacil, bromoxynil, bromoxynil octanoate, butachlor, butralin, butylate, chlomethoxyfen, chloramben, chlorbromuron, chloridazon, chlorimuron-ethyl, chlornitrofen, chlorotoluron, chlorpropham, chlorsulfuron, chlorthal-dimethyl, cinmethylin, cinosulfuron, clethodim, clomazone, clopyralid, clopyralid-olamine, cyanazine, cycloate, cyclosulfamuron, 2,4-D and its butyl, butyl, isooctyl and isopropyl esters and its dimethylammonium, diolamine and trolamine salts, daimuron, dalapon, dalapon-sodium, dazomet, 2,4-DB and its dimethylammonium, potassium and sodium salts, desmedipham, desmetryn, dicamba and its diglycolammonium, dimethylammonium, potassium and sodium salts, dichlobenil, dichlorprop, diclofop-methyl, 2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-5-methyl-3-pyridinecarboxylic acid (AC 263,222), difenzoquat metilsulfate, diflufenican, dimepiperate, dimethenamid, dimethylarsinic acid and its sodium salt, dinitramine, diphenamid, diquat dibromide, dithiopyr, diuron, DNOC, endothal, EPTC, esprocarb, ethalfluralin, ethametsulfuron-methyl, ethofumesate, ethyl α ,2-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]-4-fluorobenzenepropanoate (F8426), fenoxaprop-ethyl, fenoxaprop-P-ethyl, fenuron, fenuron-TCA, flamprop-methyl, flamprop-M-isopropyl, flamprop-M-methyl, flazasulfuron, fluazifop-butyl, fluazifop-P-butyl, fluchloralin, flumetsulam, flumiclorac-pentyl, flumioxazin, fluometuron, fluoroglycofen-ethyl, flupoxam, fluridone, flurochloridone, fluroxypyr, fomesafen, fosamine-ammonium, glufosinate, glufosinate-ammonium, glyphosate, glyphosate-isopropylammonium, glyphosate-sesquisodium, glyphosate-trimesium, halosulfuron-methyl, haloxyfop-etotyl, haloxyfop-methyl, hexazinone, imazamethabenz-methyl, imazamox (AC 299 263), imazapyr, imazaquin, imazaquin-ammonium, imazethapyr, imazethapyr-ammonium, imazosulfuron, ioxynil, ioxynil octanoate, ioxynil-sodium, isoproturon, isouron, isoxaben, isoxaflutole (RPA 201772), lactofen, lenacil, linuron, maleic hydrazide, MCPA

and its dimethylammonium, potassium and sodium salts, MCPA-isooctyl, mecoprop, mecoprop-P, mefenacet, mefluidide, metam-sodium, methabenzthiazuron, methyl [[2-chloro-4-fluoro-5-[(tetrahydro-3-oxo-1*H*,3*H*-[1,3,4]thiadiazolo[3,4-*a*]pyridazin-1-ylidene)amino]phenyl]thioacetate (KIH 9201), methylarsonic acid and its calcium, monoammonium, monosodium and disodium salts, methyl [[[1-[5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrophenyl]-2-methoxyethylidene]amino]oxy]acetate (AKH-7088), methyl 5-[[[(4,6-dimethyl-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-1-(2-pyridinyl)-1*H*-pyrazole-4-carboxylate (NC-330), metobenzuron, metolachlor, metosulam, metoxuron, metribuzin, metsulfuron-methyl, molinate, monolinuron, napropamide, naptalam, neburon, nicosulfuron, norflurazon, oryzalin, oxadiazon, 3-oxetanyl 2-[[[(4,6-dimethyl-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]benzoate (CGA 277476), oxyfluorfen, paraquat dichloride, pebulate, pendimethalin, perfluidone, phenmedipham, picloram, picloram-potassium, pretilachlor, primisulfuron-methyl, prometon, prometryn, propachlor, propanil, propaquizafop, propazine, propham, propyzamide, prosulfuron, pyrazolynate, pyrazosulfuron-ethyl, pyridate, pyrithiobac, pyrithiobac-sodium, quinclorac, quizalofop-ethyl, quizalofop-P-ethyl, quizalofop-P-tefuryl, rimsulfuron, sethoxydim, siduron, simazine, sulcotrione (ICIA0051), sulfentrazone, sulfometuron-methyl, TCA, TCA-sodium, tebuthiuron, terbacil, terbutylazine, terbutryn, thenylchlor, thiafluamide (BAY 11390), thifensulfuron-methyl, thiobencarb, tralkoxydim, tri-allate, triasulfuron, tribenuron-methyl, triclopyr, triclopyr-butotyl, triclopyr-triethylammonium, tridiphane, trifluralin, triflusaluron-methyl, and vernolate.

The compositions containing the compound of Formula I may be used to control one or more of the pathogens listed in WO 90/12791 and others, including *Alternaria cucumerina*, *Alternaria solani*, *Alternaria mali*, *Alternaria brassicola*, *Alternaria brassicae*, *Botryosphaeria obtusa*, *Bremia lectucae*, *Cercospora beticola*, *Cercospora arachidicola*, *Cercosporidium personatum*, *Cochliobolus sativus*, *Elsinoe ampelina*, *Elsinoe fawcetti*, *Fulvia fulva*, *Guignardia bidwelli*, *Gymnosporium juniperi-virginianae*, *Phomopsis viticola*, *Phytophthora nicotianae*, *Phytophthora megasperma*, *Pseudocercospora capsallae*, *Puccinia asperagi*, *Puccinia hordei*, *Ramularia beticola*, *Rhynchosporium secalis*, *Septoria apiicola*, *Septoria lycopersici*, *Septoria tritici*, *Stemphilius solani*, *Peronophora tritici*, *Mycosphaerella musicola*, *Mycosphaerella fijiensis*, *Mycosphaerella citri*, *Mycosphaerella fragariae*, *Colletotrichum* spp., *Mucor* spp., *Penicillium* spp., *Gloeosporium* spp., *Glomerella* spp., *Gnomonia* spp., *Rhizopus* spp., *Aspergillus* spp., *Xanthomonas vesicatoria*, *Pseudomonas syringae* and *Helminthosporium* spp.

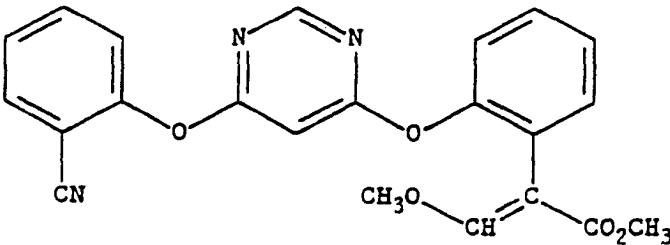
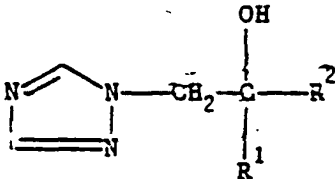
The compound of Formula I or a composition containing it as already described may be applied by land or aerial application systems, mixed with soil, peat or other rooting media for the protection of plants against seed-borne, soil-borne or foliar pathogens.

Disclosed anonymously
38829





INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : A01N 43/653 // (A01N 43/653 A01N 43:54)	A1	(11) International Publication Number: WO 93/22921 (43) International Publication Date: 25 November 1993 (25.11.93)
(21) International Application Number: PCT/GB93/00984 (22) International Filing Date: 13 May 1993 (13.05.93) (30) Priority data: 9210830.7 21 May 1992 (21.05.92) GB (71) Applicant (for all designated States except US): ZENECA LIMITED [GB/GB]; Imperial Chemical House, Millbank, London SW1P 3JF (GB). (72) Inventors; and (75) Inventors/Applicants (for US only) : BROWNELL, Keith, Harvey [US/US]; 216 Kimberley Jo Drive, Rocky Mount, NC 27804 (US). GODWIN, Jeremy, Robert [GB/GB]; 7 Wantage Road, College Town, Camberley, Surrey GU15 4DZ (GB). HEANEY, Stephen, Paul [GB/GB]; 11 Lillybrooke Crescent, Maidenhead, Berkshire SL6 3XJ (GB). SKIDMORE, Anthony, Michael [GB/GB]; 4 Liddell Close, Finchampstead, Wokingham, Berkshire RG11 4NS (GB).		(74) Agents: HOUGHTON, Malcolm, John et al.; ICI Group Patents Services Dept., Shire Park, P.O. Box 6, Bessemer Road, Welwyn Garden City, Hertfordshire AL7 1HD (GB). (81) Designated States: AU, BB, BG, BR, CA, CZ, FI, HU, JP, KP, KR, LK, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SK, UA, US, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: FUNGICIDAL COMPOSITION <div style="text-align: center;">  </div> <div style="text-align: right;">(I)</div> <div style="text-align: center;">  </div> <div style="text-align: right;">(II)</div> (57) Abstract <p>A fungicidal composition comprising a carrier or diluent; a first active ingredient which is a compound of formula (I), and a second active ingredient which is a compound of formula (II), wherein R¹ is C₁₋₄ alkyl or C₃₋₆ cycloalkyl(C₁₋₄)alkyl, and R² is phenyl or phenyl(C₁₋₄)alkyl; wherein the foregoing phenyl moieties are substituted with halogen; the relative amounts of the first and second active ingredients being such as to produce a synergistic effect.</p>		

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FUNGICIDAL COMPOSITION

The present invention relates to a fungicidal composition and to methods of using the composition to combat fungal infections of plants.

(E)-Methyl 2-[2-(6-(2-cyanophenoxy)pyrimidin-4-yloxy)phenyl]-3-methoxypropenoate, its use as a fungicide, compositions containing it, and methods of using it to combat fungal infections of plants are disclosed in EP-A2-0382375.

The present invention provides a fungicidal composition comprising a carrier or diluent; a first active ingredient which is a compound of formula (I), [(E)-methyl 2-[2-(6-(2-cyanophenoxy)pyrimidin-4-yloxy)phenyl]-3-methoxypropenoate], and a second active ingredient which is a compound of formula (II) wherein R^1 is C_{1-4} alkyl or C_{3-6} cycloalkyl(C_{1-4})alkyl; and R^2 is phenyl or phenyl(C_{1-4})alkyl; wherein the foregoing phenyl moieties are substituted with halogen; the relative amounts of the first and second active ingredients being such as to produce a synergistic effect.

Alkyl and the alkyl moieties of C_{3-6} cycloalkyl(C_{1-4})alkyl and phenyl(C_{1-4})alkyl are in the form of straight or branched chains, and are, for example, methyl, ethyl, n-butyl or tert-butyl.

Cycloalkyl is, for example, cyclopropyl.

Halogen is preferably fluorine or chlorine.

The foregoing phenyl moieties are preferably 2- or 4- monosubstituted or 2,4- disubstituted.

In one aspect the present invention provides a fungicidal composition wherein the second active ingredient is a compound of formula (II) in which R^1 is a butyl group (especially n-butyl or tert-butyl) or 1-(cyclopropyl)eth-1-yl; and R^2 is mono- or di-chlorophenyl (especially 4-chlorophenyl or 2,4-dichlorophenyl) or monochlorophenyl(C_{1-2})alkyl (especially 2-chlorobenzyl or 2-(4-chlorophenyl)eth-1-yl).

In a further aspect the compound of formula (II) is a compound wherein R^1 is n-butyl and R^2 is 2,4-dichlorophenyl, or R^1 is tert-butyl and R^2 is 2-chlorobenzyl or 2-(4-chlorophenyl)eth-1-yl.

In another aspect there is provided a composition wherein the weight ratio of the first active ingredient to the second active ingredient is in the range from 400:1 to 10:90.

In a further aspect there is provided a fungicidal composition comprising a carrier or diluent; a first active ingredient which is a compound of formula (I), and a second active ingredient which is a compound

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of formula (III); the relative amounts of the first and second active ingredients being such as to produce a synergistic effect, for example the weight ratio of the first active ingredient to the second active ingredient is in the range from 98:2 to 25:75, for example 9:1 to 25:75, and 98:2 to 9:1.

In a still further aspect there is provided a fungicidal composition comprising a carrier or diluent, a first active ingredient which is a compound of formula (I), and a second active ingredient which is a compound of formula (IV); the relative amounts of the first and second active ingredients being such as to produce a synergistic effect, for example the weight ratio of the first active ingredient to the second active ingredient is in the range from 400:1 to 10:90.

The compositions may be used to control one or more of the following pathogens: Pyricularia oryzae on rice and wheat and other Pyricularia spp. on other hosts.

Puccinia recondita, Puccinia striiformis and other rusts on wheat, Puccinia hordei, Puccinia striiformis and other rusts on barley, and rusts on other hosts e.g. turf, rye, coffee, pears, apples, peanuts, sugar beet, vegetables and ornamental plants.

Erysiphe graminis (powdery mildew) on barley, wheat, rye and turf and other powdery mildews on various hosts such as Sphaerotheca macularis on hops, Sphaerotheca fuliginea on cucurbits (e.g. cucumber), Podosphaera leucotricha on apple and Uncinula necator on vines.

Cochliobolus spp., Helminthosporium spp., Drechslera spp. (Pyrenophora spp.), Rhynchosporium spp., Septoria spp. (including Mycosphaerella graminicola and Leptosphaeria nodorum), Pseudocercospora herpotrichoides and Gaeumannomyces graminis on cereals (e.g. wheat, barley, rye), turf and other hosts.

Cercospora arachidicola and Cercosporidium personatum on peanuts and other Cercospora species on other hosts, for example, sugar beet, bananas, soya beans and rice.

Botrytis cinerea (grey mould) on tomatoes, strawberries, vegetables, vines and other hosts and other Botrytis spp. on other hosts.

Alternaria spp. on vegetables (e.g. cucumber), oil-seed rape, apples, tomatoes, cereals (e.g. wheat) and other hosts.

Venturia spp. (including Venturia inaequalis (scab)) on apples, pears, stone fruit, tree nuts and other hosts.

Cladosporium spp. on a range of hosts including cereals (e.g. wheat).

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Monilinia spp. on stone fruit, tree nuts and other hosts.

Didymella spp. on tomatoes, turf, wheat and other hosts.

Phoma spp. on oil-seed rape, turf, rice, potatoes, wheat and other hosts.

Aspergillus spp. and Aureobasidium spp. on wheat, lumber and other hosts.

Ascochyta spp. on peas, wheat, barley and other hosts.

Plasmopara viticola on vines. Other downy mildews such as Bremia lactucae on lettuce, Peronospora spp. on soybeans, tobacco, onions and other hosts, Pseudoperonospora humuli on hops and Pseudoperonospora cubensis on cucurbits.

Pythium spp. on turf and other hosts.

Phytophthora infestans on potatoes and tomatoes and other Phytophthora spp. on vegetables, strawberries, avocado, pepper, ornamentals, tobacco, cocoa and other hosts.

Thanatephorus cucumeris on rice and turf and other Rhizoctonia species on various hosts such as wheat and barley, vegetables, cotton and turf.

Sclerotinia spp. on turf, peanuts, oil-seed rape and other hosts.

Sclerotium spp. on turf, peanuts and other hosts.

Colletotrichum spp. on a range of hosts including turf, coffee and vegetables.

Laetisaria fuciformis on turf.

Mycosphaerella spp. on banana, peanut, citrus, pecan, papaya and other hosts.

Diaporthe spp. on citrus, soybean, melon, pear, lupin and other hosts.

Elsinoe spp. on citrus, vines, olives, pecans, roses and other hosts.

Pyrenopeziza spp. on oil-seed rape and other hosts.

Oncobasidium theobromae on cocoa causing vascular streak dieback.

Fusarium spp., Typhula spp., Microdochium nivale, Ustilago spp., Urocystis spp., Tilletia spp., and Claviceps purpurea on a variety of hosts but particularly wheat, barley, turf and maize.

Verticillium spp. on a range of hosts including cotton, potatoes, tomatoes and hops.

Ramularia spp. on sugar beet and other hosts.

Post-harvest diseases particularly of fruit (e.g. Pencillium digitatum and P. italicum and Trichoderma viride on oranges, Colletotrichum musae and Gloeosporium musarum on bananas and Botrytis cinerea on grapes).

Other pathogens on vines, notably Eutypa lata, Guignardia bidwellii,

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Phellinus igniarius, Phomopsis viticola, Pseudopezicula tracheiphila and Stereum hirsutum.

Other pathogens on cereals, notably Selonophoma donacis, Sclerophthora spp., Sclerospora sorghi, Nigrospora oryzae, Trichometasphaeria turcica, Cephalosporium gramineum, Epicoccum spp., Stemphylium spp., Sporobolomyces spp., Cryptosporium spp., Dilophospora alopecuri, Phaeoseptoria urvilleana, Phyllachora graminis, Omphalina pixidata and Platyspora pentamera.

Other pathogens on turf, notably Agaricus spp., Coprinus psychromorbidus, Epichloe typhina, Lepiota spp., Leptosphaeria korrae, Lycoperdon spp., Magnaporthe poae, Marasmius oreades, Myriosclerotinia borealis, Nigrospora sphaerica, Phialophora spp. and Pyricularia grisea.

Other pathogens on lumber, notably Cephaloascus fragrans, Ceratocystis spp., Chaetomium globosum, Coniophora puteana, Coriulus veriscolor, Dothiorella spp., Gliocladium virens, Gloeophyllum trabeum, Ophiostoma piceae, Penicillium spp., Phialophora spp., Phlebia gigantea, Poria placenta, Rhinocladiella atrovirens, Schizophyllum vaillantii, Sclerophoma pityophila, Sistotrema brinkmannii, Sphaeropsis sapina, Trametes veriscolor, Trichoderma pseudokoningii, Trichoderma viride and slime mould.

Fungal vectors of viral diseases e.g. Polymyxa graminis on cereals as the vector of barley yellow mosaic virus (BYMV).

Some of the compositions show a broad range of activities against fungi in vitro.

The active ingredients may move acropetally/locally in plant tissue.

The invention therefore provides a method of combating fungi which comprises applying to a plant, to a seed of a plant or to the locus of the plant or seed a fungicidally effective amount of a composition as hereinbefore defined.

It is preferred that all compositions, both solid and liquid formulations, comprise 0.0001 to 95%, more preferably 1 to 85%, for example 1 to 25% or 25 to 60%, of the first and second active ingredients combined.

When applied the foliage of plants, the compounds of the invention are applied at rates of 0.1g to 10Kg, preferably 10g to 8Kg, more preferably 10g to 4Kg, of the first and second active ingredients combined per hectare.

When used as seed dressings, the compositions of the invention are used at rates of 0.0001g (for example 0.001g or 0.05g) to 10g, preferably 0.1g to 8g, more preferably 0.1g to 4g, of the first and second active ingredients combined per kilogram of seed.

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The compositions can be applied in a number of ways. For example, they can be applied directly to the foliage of a plant, to seeds or to other medium in which plants are growing or are to be planted, or they can be sprayed on, dusted on or applied as a cream or paste formulation, or they can be applied as a vapour or as slow release granules.

Application can be to any part of the plant including the foliage, stems, branches or roots, or to soil surrounding the roots, or to the seed before it is planted, or to the soil generally, to paddy water, to irrigation water or to hydroponic culture systems. The invention compositions may also be injected into plants or sprayed onto vegetation using electrodynamic spraying techniques or other low volume methods.

The term "plant" as used herein includes seedlings, bushes and trees. Furthermore, the fungicidal method of the invention includes preventative, protectant, prophylactic and eradicant treatments.

The physical nature of the composition used in any instance will depend upon the particular purpose envisaged.

The compositions may be in the form of dustable powders or granules comprising the first and second active ingredients and a solid diluent or carrier, for example, fillers such as kaolin, bentonite, kieselguhr, dolomite, calcium carbonate, talc, powdered magnesia, fuller's earth, gypsum, diatomaceous earth and china clay. Such granules can be preformed granules suitable for application to the soil without further treatment. These granules can be made either by impregnating pellets of filler with the active ingredient or by pelleting a mixture of the active ingredient and powdered filler. Compositions for dressing seed may include an agent (for example, a mineral oil) for assisting the adhesion of the composition to the seed; alternatively the active ingredient can be formulated for seed dressing purposes using an organic solvent (for example, N-methylpyrrolidone, propylene glycol or N,N-dimethylformamide). The compositions may also be in the form of wettable powders or water dispersible granules comprising wetting or dispersing agents to facilitate the dispersion in liquids. The powders and granules may also contain fillers and suspending agents.

Compositions for pelleting seed comprise the first and second active ingredients, a solid carrier (such as clay or chalk) and a binding agent (such as a cellulosic or polysaccharide material).

The compositions may also be in the form of soluble powders or granules, or in the form of solutions in polar solvents.

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Soluble powders may be prepared by mixing the active ingredient with a water-soluble salt such as sodium bicarbonate, sodium carbonate, magnesium sulphate or a polysaccharide, and a wetting or dispersing agent to improve water dispersibility/solubility. The mixture may then be ground to a fine powder. Similar compositions may also be granulated to form water-soluble granules. Solutions may be prepared by dissolving the active ingredient in polar solvents such as ketones, alcohols and glycol ethers. These solutions may contain surface active agents to improve water dilution and prevent crystallisation in a spray tank.

Emulsifiable concentrates or emulsions may be prepared by dissolving the active ingredient in an organic solvent optionally containing a wetting or emulsifying agent and then adding the mixture to water which may also contain a wetting or emulsifying agent. Suitable organic solvents are aromatic solvents such as alkylbenzenes and alkyl naphthalenes, ketones such as cyclohexanone and methylcyclohexanone, chlorinated hydrocarbons such as chlorobenzene and trichlorethane, and alcohols such as benzyl alcohol, furfuryl alcohol, butanol and glycol ethers.

Suspension concentrates of largely insoluble solids may be prepared by ball or bead milling with a dispersing agent with a suspending agent included to stop the solid settling.

Compositions to be used as sprays may be in the form of aerosols wherein the formulation is held in a container under pressure of a propellant, e.g. fluorotrichloromethane or dichlorodifluoromethane.

The first and second active ingredients can be mixed in the dry state with a pyrotechnic mixture to form a composition suitable for generating in enclosed spaces a smoke containing the active ingredients.

Alternatively, the compositions may be used in micro-encapsulated form. They may also be formulated in biodegradable polymeric formulations to obtain a slow, controlled release of the active substance.

By including suitable additives, for example additives for improving the uptake, distribution, adhesive power and resistance to rain on treated surfaces, the different compositions can be better adapted for various utilities. Other additives may be included to improve the biological efficacy of the various formulations. Such additives can be surface active materials to improve the wetting and retention on surfaces treated with the formulation and also the uptake and mobility of the active material, or additionally can include oil based spray additives, for example, certain mineral oil and natural plant oil (such as soya bean and rape seed oil)

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additives, or blends of them with other adjuvants, have been found to enhance several-fold foliar activity against, for example, Puccinia hordei.

The invention compositions can be used as mixtures with fertilisers (e.g. nitrogen-, potassium- or phosphorus-containing fertilisers). Granules comprising only pieces of fertiliser incorporating, for example coated with, the composition are preferred. Such granules suitably contain up to 25% by weight of the first and second active ingredients. The invention therefore also provides a fertiliser and a composition of the invention.

Wettable powders, emulsifiable concentrates and suspension concentrates will normally contain surfactants, e.g. a wetting agent, dispersing agent, emulsifying agent or suspending agent. These agents can be cationic, anionic or non-ionic agents.

Suitable cationic agents are quaternary ammonium compounds, for example, cetyltrimethylammonium bromide. Suitable anionic agents are soaps, salts of aliphatic monoesters of sulphuric acid (for example, sodium lauryl sulphate), and salts of sulphonated aromatic compounds (for example, sodium dodecylbenzenesulphonate, sodium, calcium or ammonium lignosulphonate, butylnaphthalene sulphonate, and a mixture of sodium diisopropyl- and triisopropylnaphthalene sulphonates).

Suitable non-ionic agents are the condensation products of ethylene oxide with fatty alcohols such as oleyl or cetyl alcohol, or with alkyl phenols such as octyl- or nonylphenol and octylcresol. Other non-ionic agents are the partial esters derived from long chain fatty acids and hexitol anhydrides, the condensation products of the said partial esters with ethylene oxide, and the lecithins. Suitable suspending agents are hydrophilic colloids (for example, polyvinylpyrrolidone and sodium carboxymethylcellulose), and swelling clays such as bentonite or attapulgite.

Compositions for use as aqueous dispersions or emulsions are generally supplied in the form of a concentrate containing a high proportion of the active ingredient, the concentrate being diluted with water before use. These concentrates should preferably be able to withstand storage for prolonged periods and after such storage be capable of dilution with water in order to form aqueous preparations which remain homogeneous for a sufficient time to enable them to be applied by conventional spray equipment. The concentrates may conveniently contain up to 95%, suitably 1-85%, for example 1-25% or 25-60%, by weight of the active ingredients.

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After dilution to form aqueous preparations, such preparations may contain varying amounts of the active ingredient depending upon the intended purpose, but an aqueous preparation containing 0.0001 to 10%, for example 0.005 to 10%, by weight of active ingredient may be used.

The compositions of this invention may contain other compounds having biological activity, e.g. compounds having similar or complementary fungicidal activity or which possess plant growth regulating, herbicidal or insecticidal activity.

An additional fungicidal compound may be present in the composition of the invention. By including another fungicide, the resulting composition can have a broader spectrum of activity or a greater level of intrinsic activity than the composition of the invention alone. Examples of fungicidal compounds which may be included in the composition of the invention are (+)-cis-1-(4-chlorophenyl)-2-(1H-1,2,4-triazol-1-yl)-cycloheptanol, (2RS,3RS)-1-[3-(2-chlorophenyl)-2-(4-fluorophenyl)-oxiran-2-ylmethyl]-1H-1,2,4-triazole, (RS)-1-aminopropylphosphonic acid, (RS)-4-(4-chlorophenyl)-2-phenyl-2-(1H-1,2,4-triazol-1-ylmethyl)butyronitrile, (Z)-N-but-2-enyloxymethyl-2-chloro-2',6'-diethylacetanilide, 1-(2-cyano-2-methoxyiminoacetyl)-3-ethyl urea, 3-(2,4-dichlorophenyl)-2-(1H-1,2,4-triazol-1-yl)quinazolin-4(3H)-one, 4-(2,2-difluoro-1,3-benzodioxol-4-yl)pyrrole-3-carbonitrile, 4-bromo-2-cyano-N,N-dimethyl-6-trifluoromethylbenzimidazole-1-sulphonamide, 5-ethyl-5,8-dihydro-8-oxo-(1,3)-dioxol-(4,5-g)quinoline-7-carboxylic acid, α -[N-(3-chloro-2,6-xyl-yl)-2-methoxyacetamido]- γ -butyrolactone, alanycarb, aldimorph, ampropylfos, anilazine, azaconazole, BAS 490F, benalaxyl, benomyl, biloxazol, binapacryl, bitertanol, blasticidin S, bromuconazole, bupirimate, butenachlor, buthiobate, captafol, captan, carbendazim, carbendazim chlorhydrate, carboxin, chinomethionate, chlorbenzthiazone, chloroneb, chlorothalonil, chlorozolinate, clozylacon, copper containing compounds such as copper oxychloride, copper oxyquinolate, copper sulphate and Bordeaux mixture, cycloheximide, cymoxanil, cyproconazole, cyprofuram, di-2-pyridyl disulphide 1,1'-dioxide, dichlofluanid, dichlone, diclobutrazol, diclomezine, dicloran, didecyl dimethyl ammonium chloride, diethofencarb, difenoconazole, O,O-di-iso-propyl-S-benzyl thiophosphate, dimefluazole, dimetconazole, dimethomorph, dimethirimol, diniconazole, dinocap, dipyrithione, ditalimfos, dithianon, dodemorph, dodine, doguadine, edifenphos, epoxiconazole, etaconazole, ethirimol, ethoxyquin, ethyl (Z)-N-benzyl-N-([methyl(methyl-thioethylideneamino-oxycarbonyl)amino]thio)-

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- β -alaninate, etridiazole, fenaminosulph, fenapanil, fenarimol, fenbuconazole, fenfuram, fempiclonil, fenpropidin, fenpropimorph, fentin acetate, fentin hydroxide, ferbam, ferimzone, fluazinam, fluoroimide, fluotrimazole, flutolanil, flutriafol, flusilazole, folpet, fuberidazole, furalaxyl, furconazole-cis, guazatine, hydroxyisoxazole, hymexazole, imazalil, imibenconazole, ipconazole, iprobenfos, iprodione, isopropanyl butyl carbamate, isoprothiolane, kasugamycin, mancozeb, maneb, mepanipyrim, mepronil, metalaxyl, metconazole, methfuroxam, metiram, metiram-zinc, metsulfovax, myclobutanil, neoasozin, nickel dimethyldithiocarbamate, nitrothal-isopropyl, nuarimol, ofurace, organomercury compounds, oxadixyl, oxolinic acid, oxycarboxin, pefurazoate, penconazole, pencycuron, phenazin oxide, phosetyl-Al, phosphorus acids, phthalide, polyoxin D, polyram, probenazole, prochloraz, procymidone, propamocarb, propamocarb hydrochloride, propiconazole, propineb, propionic acid, prothiocarb, pyracarbolid, pyrazophos, pyrifenox, pyroquilon, pyroxyfur, pyrrolnitrin, quaternary ammonium compounds, quinconazole, quinomethionate, quintozone, rabenazole, sodium pentachlorophenate, SSF 126, streptomycin, sulphur, tebuconazole, techlofthalam, tecnazene, tetraconazole, thiabendazole, thicarbanil, thicyofen, 2-(thiocyanomethylthio)benzothiazole thiophanate-methyl, thiram, timibenconazole, tolclofos-methyl, tolylfluanid, triacetate salt of 1,1'-iminodi-(octamethylene)diguandine, triadimefon, triadimenol, triazbutyl, triazoxide, tricyclazole, tridemorph, triforine, triflumizole, triticonazole, validamycin A, vapam, vinclozolin, zineb and ziram. The compounds of general formula (I) can be mixed with soil, peat or other rooting media for the protection of plants against seed-borne, soil-borne or foliar fungal diseases.

Suitable insecticides which may be incorporated in a composition of the present invention include natural pyrethrins or pyrethroids such as permethrin, fenvalerate, deltamethrin, cyhalothrin, lambda-cyhalothrin, cypermethrin, α - and β -cypermethrin, cycloprothrin, tefluthrin, empenthrin, ethofenprox, tetramethrin, bioallethrin, fenfluthrin, prallethrin, 5-benzyl-3-furylmethyl (E)-(1R,3S)-2,2-dimethyl-3-(2-oxothioloan-3-yl-idenemethyl)cyclopropane carboxylate and pentafluorobenzyl (cis)-3-[2-fluoro-2-(methoxycarbonyl)ethenyl]-2,2-dimethylcyclopropane carboxylate; organophosphates such as profenofos, propaphos, sulprofos, dichlorvos, methyl parathion, azinphos-methyl, demeton-s-methyl, heptenophos, thiometon, fenamiphos, monocrotophos, triazophos, methamidophos, dimethoate, phenthoate, phosphamidon, malathion,

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chlorpyrifos, phosalone, fensulphothion, fenthion, formothion, isoxathion, fonofos, phorate, phoxim, pyrimiphos-methyl, fenitrothion and diazinon; carbamates (including aryl carbamates) such as pirimicarb, cloethocarb, carbofuran, carbonyl, isoprocarb, ethiofencarb, aldicarb, thiofurox, carbosulfan, bendiocarb, fenobucarb, propoxur, oxamyl and XMC; benzoyl ureas such as triflumuron and chlorofluazuron; organic tin compounds such as cyhexatin, fenbutatin oxide and azocyclotin; macrolides such as avermectins or milbemycins, for example abamectin, avermectin and milbemycin; hormones and synthetic mimics thereof such as juvenile hormone, juvabione, ecdysones, methoprene and hydroprene; pheromones; and organochlorine compounds such as benzene hexachloride, DDT, chlordane, dieldrin and endosulfan.

In addition to the major chemical classes of insecticide listed above, other insecticides having particular targets may be employed in the mixture an appropriate. For instance selective insecticides for particular crops, for example stem borer specific insecticides for use in rice such as cartap or buprofezin, can be employed. Alternatively, insecticides or acaricides specific for the control of specific insect growth stages, for example ovolarvicides such as clofentezine, amitraz, chlordimeform, flubenzimine, hexythiazox and tetradifon; motilicides such as dicofol or propargite; adulticides such as bromopropylate, chlorobenzilate; or insect growth regulators such as hydramethylnon, cyromazine, methoprene, chlorfluazuron and diflubenzuron may also be included in the compositions.

Examples of suitable insecticide synergists for use in the compositions include piperonyl butoxide, sesamex and dodecyl imidazole.

Plant growth regulating compounds are compounds which control weeds or seedhead, formation, or selectively control the growth of less desirable plants (e.g. grasses).

Examples of suitable plant growth regulating compounds for use in the compositions of the present invention are 1-(4-chlorophenyl)-4,6-di-methyl-2-oxo-1,2-dihydropyridine-3-carboxylic acid; methyl-3,6-dichloroanisate; abscisic acid; daminozide; difenzoquat; dikegulac; ethephon; fenpentezol; fluoridamid; inabenfide; isopyrimol; long chain fatty alcohols and acids; maleic hydrazide; mefluidide; fenchlorazole-ethyl; chloine chloride; ethephon; morphactins (e.g. chlorfluoroecol); paclobutrazol; substituted benzoic acid (e.g. triiodobenzoic acid); substituted quaternary ammonium and phosphonium compounds (e.g. chloromequat, chlorphonium or mepiquat chloride); tecnazene; the auxins (e.g. indoleacetic acid, indolebutyric

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acid, naphthylacetic acid or naphthoxyacetic acid); the cytokinins (e.g. benzimidazole, benzyladenine, benzylaminopurine, diphenylurea or kinetin); the gibberellins (e.g. GA₃, GA₄ or GA₇); triapenthenol; benzo-2,1,3-thiadiazin-4-one-2,2-dioxides such as bentazone; hormone herbicides, particularly the phenoxy alkanolic acids such as MCPA, MCPA-thioethyl, dichlorprop, 2,4,5-T, MCPB, 2,4-D, 2,4-DB, mecoprop, trichlopyr, fluroxypyr, clopyralid, and their derivatives (eg. salts, esters and amides); 1,3 dimethylpyrazole derivatives such as pyrazoxyfen, pyrazolate and benzofenap; Dinitrophenols and their derivatives (eg. acetates) such as dinoterb, dinoseb and its ester, dinoseb acetate; dinitroaniline herbicides such as dinitramine, trifluralin, ethalfluorol, pendimethalin, oryzalin; arylurea herbicides such as diuron, flumeturon, metoxuron, neburon, isoproturon, chlorotoluron, chloroxuron, linuron, monolinuron, chlorobromuron, daimuron, methabenzthiazuron; phenylcarbamoyloxyphenylcarbamates such as phenmedipham and desmedipham; 2-phenylpyridazin-3-ones such as chloridazon and norflurazon; uracil herbicides such as lenacil, bromacil and terbacil; triazine herbicides such as atrazine, simazine, aziprotryne, cyanazine, prometryn, dimethametryn, simetryne, and terbutryn; phosphorothioate herbicides such as piperophos, bensulide, and butamifos; thiolcarbamate herbicides such as cycloate, vernolate, molinate, thiobencarb, butylate*, EPTC*, tri-allate, di-allate, esprocarb, thiocarbazil, pyridate, and dimepiperate; 1,2,4-triazin-5-one herbicides such as metamitron and metribuzin; benzoic acid herbicides such as 2,3,6-TBA, dicamba and chloramben; anilide herbicides such as pretilachlor, butachlor, alachlor, propachlor, propanil, metazachlor, metolachlor, acetochlor, and dimethachlor; dihalobenzonitrile herbicides such as dichlobenil, bromoxynil and ioxynil; haloalkanoic herbicides such as dalapon, TCA and salts thereof; diphenylether herbicides such as lactofen, fluroglycofen or salts or ester thereof, nitrofen, bifenox, acifluorfen and salts and esters thereof, oxyfluorfen, fomesafen, chlornitrofen and chlomethoxyfen; phenoxyphenoxypropionate herbicides such as diclofop and esters thereof such as the methyl ester, fluazifop and esters thereof, benzoilprop and esters thereof, haloxyfop and esters thereof, quizalofop and esters thereof and fenoxaprop and esters thereof such as the ethyl ester; cyclohexanedione herbicides such as alloxymid and salts thereof, sethoxydim, cycloxydim, tralkoxydim, and clethodim; sulfonyl urea herbicides such as chlorosulfuron, sulfometuron, metsulfuron and esters thereof; benzsulfuron and esters thereof such as DPX-M6313,

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chlorimuron and esters such as the ethyl ester thereof pirimisulfuron and esters such as the methyl ester thereof, 2-[3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-3-methylureido-sulphonyl] benzoic acid esters such as the methyl ester thereof (DPX-LS300) and pyrazosulfuron; imidazolidinone herbicides such as imazaquin, imazamethabenz, imazapyr and isopropylammonium salts thereof, imazethapyr; arylanilide herbicides such as flamprop and esters thereof, benzoylprop-ethyl, diflufenican; amino acid herbicides such as glyphosate and glufosinate and their salts and esters, sulphasate and bialaphos; organoarsenical herbicides such as monosodium methanearsonate (MSMA); herbicidal amide derivative such as napropamide, propyzamide, asulam, carbetamide, tebutam, bromobutide, isoxaben, naproanilide and naptalam; miscellaneous herbicides including ethofumesate, cinmethylin, difenzoquat and salts thereof such as the methyl sulphate salt, clomazone, oxadiazon, bromofenoxim, barban, tridiphane, flurochloridone, quinclorac, dithiopyr and mefanacet; and contact herbicides (such as bipyridylum herbicides for example those in which the active entity is paraquat and those in which the active entity is diquat), and mixtures of any of the foregoing. (* These compounds are preferably employed in combination with a safener such as dichlormid.)

The following Examples illustrate the invention.

EXAMPLE 1

Testing of a composition of the invention against Puccinia hordei (barley brown rust) in a field test on barley in test area 20m² (four replicates).

The compounds were applied as suspension concentrate formulations with a tank-mixed adjuvant and were diluted with water to the required concentration.

The compounds were applied using knapsack sprayers in a water volume of 300 l/ha. Two applications were made between GSZ 30 and GSZ 65 depending upon disease pressure and local recommendations (GSZ = Zadoks Growth Stage). Disease control was assessed as percentage brown rust on specific leaves by visual estimation of 25 tillers per plot.

Results are expressed as mean absolute percentage disease levels, and untreated plots had a mean absolute disease level of 80.40%.

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Application rate g ai/ha		Mean absolute disease level (on leaf 2; 15 days after application 2)
Compound (I)	Compound (IV)	
25	0	33.51%
0	31.25	26.76%
25	31.25	6.65%

EXAMPLE 2

Testing of a composition of the invention against Venturia inaequalis (apple scab).

Young apple seedlings were grown in 3.8cm (1.5") diameter plastic pots containing John Innes Potting Compost (No. 1).

The test compounds, formulated as suspension concentrates or a solution in acetone, were diluted in water to the required concentration immediately before application.

The test compounds were applied to the underside of the apple seedling leaves either one day before (protectant) or three days after (eradicant) a suspension of Venturia inaequalis spores was applied to the same surface.

After inoculation, the plants were put into an appropriate environment to allow infection to proceed and then incubated until the disease was ready for assessment (10-12 days after inoculation). Venturia inaequalis infection was assessed as the percentage area of sporulating disease on a leaf in comparison with the untreated control. Four replicate plants were assessed per treatment.

Eradicant Treatment

Application rate ppm ai		Percentage area of sporulating disease
Compound (I)	Compound (III)	
0.2	0	70.7
0	0.2	76.9
0.2	0.2	14.1

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Protectant Treatment

Application rate ppm ai		Percentage area of sporulating disease
Compound (I)	Compound (III)	
0.2	0	74.5
0	0.2	109
0.2	0.2	20.4

These Examples give data for the two components present in the compositions. By using Limpel's formula, these data demonstrate that the observed activity of the compositions comprising two active ingredients is greater than would be expected.

Limpel's formula (Pesticide Science (1987) 19 309-315 at 312) is:

$$E = X+Y - \frac{XY}{100}$$

in which

E is the expected fungicidal activity of substances A+B at p+q Kg/ha;

X is the percentage fungicidal activity of substance A at a rate of p kg active ingredient/ha; and

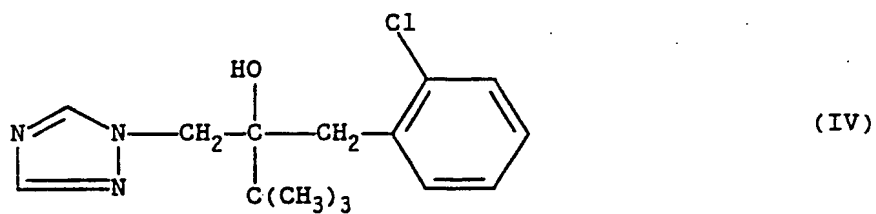
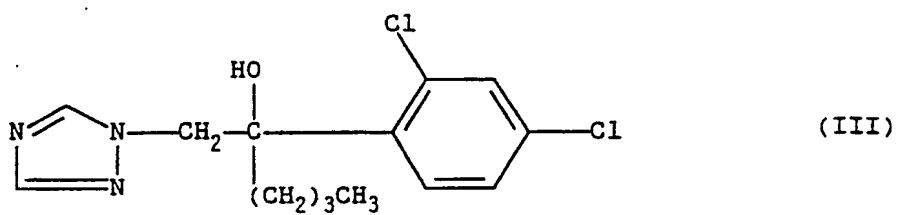
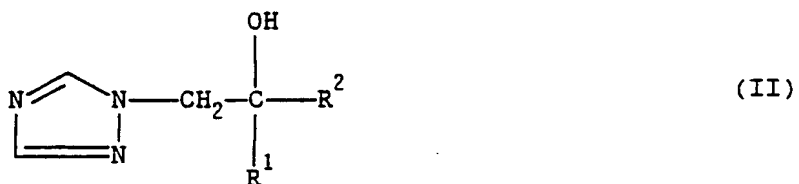
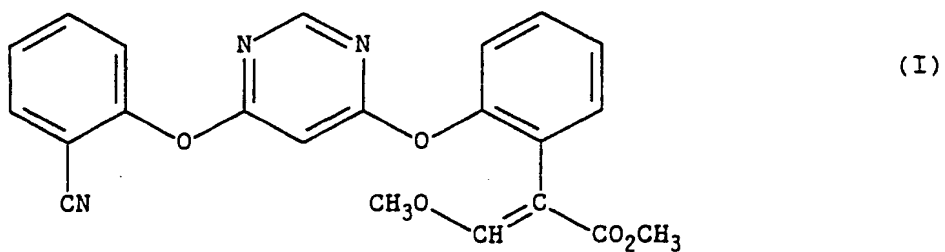
Y is the percentage fungicidal activity of substance B at a rate of q kg active ingredient/ha.

If the fungicidal activity observed is greater than the value E calculated according to Limpel, then the combination of A and B is synergistic.

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CHEMICAL FORMULAE

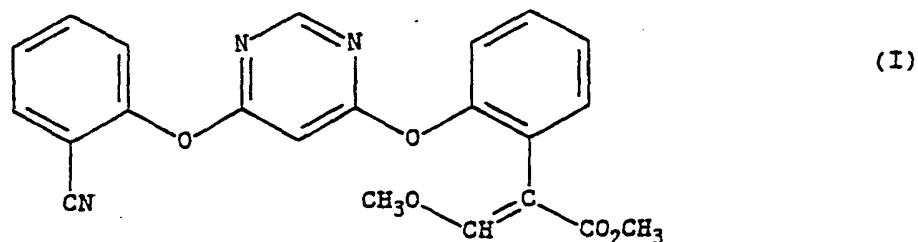
(IN DESCRIPTION)



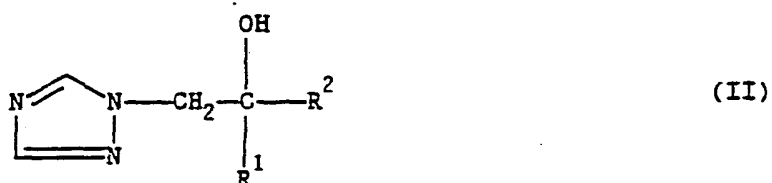
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CLAIMS

1. A fungicidal composition comprising a carrier or diluent; a first active ingredient which is a compound of formula (I):

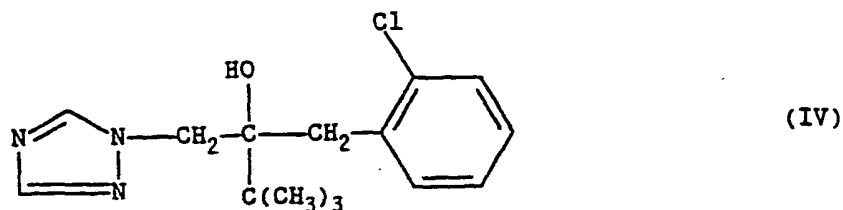
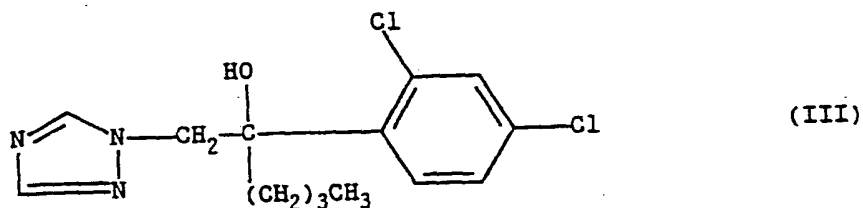


and a second active ingredient which is a compound of formula (II):



wherein R^1 is C_{1-4} alkyl or C_{3-6} cycloalkyl(C_{1-4})alkyl; and R^2 is phenyl or phenyl(C_{1-4})alkyl; wherein the foregoing phenyl moieties are substituted with halogen; the relative amounts of the first and second active ingredients being such as to produce a synergistic effect.

2. A fungicidal composition as claimed in claim 1 wherein the second active ingredient is a compound of formula (III) or (IV).



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3. A method of combating fungal infections of plants comprising applying to the plant, to the seed of the plant or to the locus of the plant or seed a composition as claimed in claim 1.
4. A method of combating fungal infections of plants caused by Puccinia spp, the method comprising applying to the plant, to the seed of the plant or to the locus of the plant or seed a fungicidal composition comprising a diluent or carrier; a first active ingredient which is a compound of formula (I); and a second active ingredient which is a compound of formula (IV); the relative amounts of the first and second active ingredients being such as to produce a synergistic effect.
5. A method of combating fungal infections of plants caused by Venturia spp, the method comprising applying to the plant, to the seed of the plant or to the locus of the seed or plant a fungicidal composition comprising a diluent or carrier; a first active ingredient which is a compound of formula (I); and a second active ingredient which is a compound of formula (III); the relative amounts of the first and second active ingredients being such as to produce a synergistic effect.
6. A composition as claimed in claim 1 or 2 or a composition as used in claim 4 or 5 wherein the weight ratio of the first active ingredient to the second active ingredient is in the range from 400:1 to 10:90.
7. A method of combating fungal infections of plants comprising applying to a plant, to the seed of a plant or to the locus of a seed or plant a fungicidally effective amount of a composition as claimed in claim 1.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 93/00984

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate)		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 A01N43/653; //(A01N43/653,43:54)		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	A01N	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	EP,A,0 382 375 (IMPERIAL CHEMICAL INDUSTRIES) 16 August 1990 cited in the application see page 3, line 1 - line 37 see page 5; table 1; compound no. 9 see page 29, line 51 - page 30, line 26 ---	1-5,7
P,X	RESEARCH DISCLOSURE no. 338, 10 June 1992, HAVANT GB pages 506 - 510 ANONYMOUS 'Mixtures of Fungicides and Insecticides' disclosure no. 33893 --- -/--	1-7
¹⁰ Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
27 JULY 1993	06.08.93	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	LAMERS W.	

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED TO BE RELEVANT

(CONTINUED FROM THE SECOND SHEET)

Category ^o	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
P,X	DATABASE WPIL Week 9313, Derwent Publications Ltd., London, GB; AN 93-107493 see abstract & RESEARCH DISCLOSURE no. 346, 10 February 1993, HAVANT GB ANONYMOUS 'Fungicidal mixts. - contg. E-me thyl(((cyano:phenoxy)pyrimidinyl:oxy)pheny l)methoxy:propenoate and further fungicides' disclosure no. 346121 -----	1,2,7
A	EP,A,0 415 569 (IMPERIAL CHEMICAL INDUSTRIES) 6 March 1991 see page 2, line 1 - line 3 see page 3, line 22 - page 4, line 5 see page 8, line 54 -----	1-7

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

GB 9300984
SA 73705

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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27/07/93

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0382375	16-08-90	AU-B- 625501	16-07-92
		AU-A- 4905290	16-08-90
		CN-A- 1047286	28-11-90
		US-A- 5145856	08-09-92

EP-A-0415569	06-03-91	AU-A- 6022090	07-03-91
		CN-A- 1049771	13-03-91
		JP-A- 3193705	23-08-91

EPO FORM P0479

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : A01N 43/54 // (A01N 43/54, 61:00, 55:00, 47:38, 43:84, 43:653, 43:54, 37:50)	A1	(11) International Publication Number: WO 98/33381 (43) International Publication Date: 6 August 1998 (06.08.98)
(21) International Application Number: PCT/US98/01381 (22) International Filing Date: 26 January 1998 (26.01.98) (30) Priority Data: 60/036,063 30 January 1997 (30.01.97) US (71) Applicant (for all designated States except US): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): CROMPTON, Martina, Cajnar [US/US]; 6178 Telegraph Road, Elkton, MD 21921 (US). FOOR, Stephen, Ray [US/US]; 508 Hemingway Drive, Hockessin, DE 19707 (US). JULIS, Anthony, Jay [US/US]; 2706 Doris Drive, Wilmington, DE 19803 (US). (74) Agent: HEISER, David, E.; E.I. du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: AL, AM, AU, AZ, BA, BB, BG, BR, BY, CA, CN, CU, CZ, EE, GE, GW, HU, ID, IL, IS, JP, KG, KP, KR, KZ, LC, LK, LR, LT, LV, MD, MG, MK, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, SL, TJ, TM, TR, TT, UA, US, UZ, VN, YU, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: FUNGICIDAL MIXTURES (57) Abstract <p>Advantageous combinations are disclosed comprising (1) at least one compound selected from the quinazolinones of Formula (I), <i>N</i>-oxides and agriculturally suitable salts thereof and (2) at least one compound selected from: (a) compounds acting at the <i>bc₁</i> complex of the fungal mitochondrial respiratory electron transfer site and (b) compounds that control fungal disease by inhibiting sterol biosynthesis. D is O or S and R¹-R⁴ are as defined in the disclosure. Included are fungicidal compositions comprising fungicidally effective amounts of the compound combinations of the invention and a method for controlling plant diseases caused by fungal plant pathogens comprising applying to the plant or portion thereof, or to the plant seed or seedling, a fungicidally effective amount of the compound combinations of the invention.</p> <div style="text-align: center;"> <p style="margin-left: 100px;">(I)</p> </div>		

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DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

TITLE

FUNGICIDAL MIXTURES

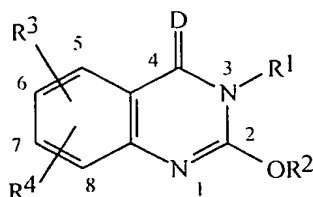
BACKGROUND OF THE INVENTION

Fungicides that effectively control plant diseases are in constant demand by
5 growers. Plant diseases are highly destructive, difficult to control and quickly develop
resistance to commercial fungicides. Combinations of pesticides are often used to
facilitate disease control, to broaden spectrum of control and to retard resistance
development. It is recognized in the art that the advantages of particular pesticide
combinations can often vary, depending on such factors as the particular plant and plant
10 disease to be treated, and the treatment conditions. Accordingly, there is an ongoing
search for advantageous combinations of pesticides.

International Patent Application WO 94/26722 discloses certain quinazolinone
compounds as fungicides (e.g., 6-bromo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone,
6,8-diiodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone and 6-iodo-3-propyl-2-
15 propyloxy-4(3*H*)-quinazolinone). International Patent Application WO 95/14009
discloses certain triazolone fungicides (e.g., 2,4-dihydro-5-methoxy-2-methyl-4-[2-
[[[1-[3-(trifluoromethyl)phenyl]ethylidene]amino]oxy]-methyl]phenyl]-3*H*-1,2,4-
triazol-3-one). Kresoxim-methyl (BAS 490F) is a fungicide under consideration for the
control of plant diseases, especially fungal diseases of wheat, grapes and fruits. (See E.
20 Ammermann, G. Lorenz, K. Schelberger, B. Wenderoth, H. Sauter and C. Rentzea
"BAS 490F - A Broad-Spectrum Fungicide with a New Mode of Action" in *Brighton
Crop Protection Conference - Pests and Diseases* - 1992, 1, 403-410.) Azoxystrobin
(ICIA5504) is a fungicide under consideration for the control of plant diseases on a wide
range of crops. (See J. R. Godwin, V. M. Anthony, J. M. Clough and C. R. A. Godfrey
25 "ICIA5504: A Novel, Broad Spectrum, Systemic β -Methoxyacrylate Fungicide" in
Brighton Crop Protection Conference - Pests and Diseases - 1992, 1, 435-442.)
European Patent Application EP-A-398,692 discloses (*E*)-2-(methoxyimino)-*N*-methyl-
2-(2-phenoxyphenyl)acetamide also known as SSF 126. This fungicide is under
consideration for the control of plant disease, especially of rice. EP-A-68813 discloses
30 certain triazole compounds as fungicides (e.g., flusilazole). EP-A-40345 discloses
certain triazole compounds as fungicides (e.g., tebuconazole).

SUMMARY OF THE INVENTION

This invention is directed to fungicidal combinations (e.g., mixtures) comprising (1) at least one compound selected from the quinazolinones of Formula I (including all geometric and stereoisomers), *N*-oxides, and agriculturally suitable salts thereof,



I

wherein

D is O or S;

R¹ is C₁-C₁₀ alkyl; C₃-C₅ cycloalkyl; C₃-C₁₀ alkenyl; C₃-C₁₀ alkynyl;
 C₁-C₁₀ haloalkyl; C₃-C₁₀ haloalkenyl; C₃-C₁₀ haloalkynyl;
 C₂-C₁₀ alkoxyalkyl; C₂-C₁₀ alkylthioalkyl; C₂-C₁₀ alkylsulfinylalkyl;
 C₂-C₁₀ alkylsulfonylalkyl; C₄-C₁₀ cycloalkylalkyl;
 C₄-C₁₀ alkenyloxyalkyl; C₄-C₁₀ alkynyloxyalkyl; C₄-C₁₀
 (cycloalkyl)oxyalkyl; C₄-C₁₀ alkenylthioalkyl; C₄-C₁₀ alkynylthioalkyl;
 C₄-C₁₀ (cycloalkyl)thioalkyl; C₂-C₁₀ haloalkoxyalkyl;
 C₄-C₁₀ haloalkenyloxyalkyl; C₄-C₁₀ haloalkynyloxyalkyl;
 C₄-C₁₀ alkoxyalkenyl; C₄-C₁₀ alkoxyalkynyl; C₄-C₁₀ alkylthioalkenyl;
 C₄-C₁₀ alkylthioalkynyl; C₄-C₁₀ trialkylsilylalkyl; C₁-C₁₀ alkyl substituted
 with NR⁵R⁶, nitro, cyano or phenyl optionally substituted with R⁸, R⁹ and
 R¹⁰; C₁-C₁₀ alkoxy; C₁-C₁₀ haloalkoxy; C₁-C₁₀ alkylthio;
 C₁-C₁₀ haloalkylthio; or pyridinyl, furanyl, thienyl, naphthalenyl,
 benzofuranyl, benzothienyl or quinolinyl each optionally substituted with
 R⁸, R⁹ and R¹⁰;

R² is C₁-C₁₀ alkyl; C₃-C₇ cycloalkyl; C₃-C₁₀ alkenyl; C₃-C₁₀ alkynyl;
 C₁-C₁₀ haloalkyl; C₃-C₁₀ haloalkenyl; C₃-C₁₀ haloalkynyl;
 C₂-C₁₀ alkoxyalkyl; C₂-C₁₀ alkylthioalkyl; C₂-C₁₀ alkylsulfinylalkyl;
 C₂-C₁₀ alkylsulfonylalkyl; C₄-C₁₀ cycloalkylalkyl;
 C₄-C₁₀ alkenyloxyalkyl; C₄-C₁₀ alkynyloxyalkyl; C₄-C₁₀
 (cycloalkyl)oxyalkyl; C₄-C₁₀ alkenylthioalkyl; C₄-C₁₀ alkynylthioalkyl;
 C₄-C₁₀ (cycloalkyl)thioalkyl; C₂-C₁₀ haloalkoxyalkyl;
 C₄-C₁₀ haloalkenyloxyalkyl; C₄-C₁₀ haloalkynyloxyalkyl;
 C₄-C₁₀ alkoxyalkenyl; C₄-C₁₀ alkoxyalkynyl; C₄-C₁₀ alkylthioalkenyl;
 C₄-C₁₀ alkylthioalkynyl; C₄-C₁₀ trialkylsilylalkyl; C₂-C₁₀ cyanoalkyl;

C₁-C₁₀ nitroalkyl; C₁-C₁₀ alkyl substituted with CO₂R⁵, NR⁵R⁶, or phenyl optionally substituted with R⁷, R⁹ and R¹⁰; phenyl optionally substituted with R⁷, R⁹ and R¹⁰; -N=CR⁵R⁵; or -NR⁵R⁶; or

R¹ and R² are taken together to form -CH₂(CH₂)_qCH₂-;

5 q is 0, 1, 2, 3 or 4;

R³ is halogen, C₁-C₈ alkyl, C₃-C₈ cycloalkyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₁-C₈ haloalkyl, C₃-C₈ haloalkenyl, C₃-C₈ haloalkynyl, C₁-C₈ alkoxy, C₁-C₈ haloalkoxy, C₃-C₈ alkenyloxy, C₃-C₈ alkynyloxy, C₁-C₈ alkylthio, C₃-C₈ alkenylthio, C₃-C₈ alkynylthio, C₁-C₈ alkylsulfinyl, C₁-C₈ alkylsulfonyl, C₂-C₈ alkoxyalkyl, C₂-C₈ alkylthioalkyl, C₂-C₈ alkylsulfinylalkyl, C₂-C₈ alkylsulfonylalkyl, C₄-C₈ cycloalkylalkyl, C₃-C₈ trialkylsilyl, NR⁵R⁶, C₅-C₈ trialkylsilylalkynyl or phenyl optionally substituted with at least one R⁷;

10 R⁴ is hydrogen, halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy or C₁-C₄ haloalkoxy;

each R⁵ is independently hydrogen, C₁-C₄ alkyl or phenyl optionally substituted with at least one R⁷;

each R⁶ is independently hydrogen, C₁-C₈ alkyl or phenyl optionally substituted with at least one R⁷; or

20 when R⁵ and R⁶ are attached to the same nitrogen atom, R⁵ and R⁶ can be taken together to form -CH₂CH₂CH₂CH₂-, -CH₂(CH₂)₃CH₂-, -CH₂CH₂OCH₂CH₂-, -CH₂CH(Me)CH₂CH(Me)CH₂- or -CH₂CH(Me)OCH(Me)CH₂-;

25 each R⁷ is independently halogen, C₁-C₄ alkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkyl, nitro or cyano;

R⁸ is C₁-C₆ alkyl, C₁-C₆ alkoxy, C₁-C₆ haloalkyl, halogen, C₂-C₈ alkynyl, C₁-C₆ alkylthio, phenyl or phenoxy each optionally substituted with at least one R⁷, cyano, nitro, C₁-C₆ haloalkoxy, C₁-C₆ haloalkylthio, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, acetyl, CO₂Me or N(C₁-C₂ alkyl)₂;

30 each R⁹ is independently methyl, ethyl, methoxy, methylthio, halogen or trifluoromethyl; and

each R¹⁰ is independently halogen;

and (2) at least one compound selected from (a) compounds acting at the bc₁ complex of the fungal mitochondrial respiratory electron transfer site and (b) compounds that control fungal disease by inhibiting the sterol biosynthesis pathway. This invention provides agricultural compositions containing these combinations and the use of the combinations as fungicides. Advantageous compositions include those where component (1) and component (2) are present in a fungicidally effective amount and the

mole ratio of component (1) to component (2) is from about 30:1 to 1:30.

Advantageous methods include those where component (1) and component (2) are added in amounts sufficient to provide a fungicidal effectiveness greater than the sum of the fungicidal effectivenesses provided by those amounts of said components taken independently.

DETAILS OF THE INVENTION

Combinations of fungicides are used in accordance with this invention to facilitate disease control and to retard resistance development. Suitable compositions and methods are provided.

For example, this invention also provides methods for controlling plant diseases caused by fungal plant pathogens comprising applying to the plant or portion thereof to be protected, or to the plant seed or seedling to be protected one of the following:

A) an effective amount of a fungicidal composition comprising component (1), component (2), and at least one of a surfactant, a solid diluent or a liquid diluent;

B) (i) an effective amount of a first composition comprising component (1), and at least one of a surfactant, solid or liquid diluent; and (ii) an effective amount of a second composition comprising component (2), and at least one of a surfactant, a solid diluent or a liquid diluent; said first and second compositions applied sequentially in any order; or

C) an effective amount of a physical mixture of the first and second compositions as defined in B above.

The mole ratio of the compound(s) of component (1) to the compound(s) of component (2) applied is normally from about 30:1 to 1:30, and the compound(s) of component (1) and the compound(s) of component (2) are normally applied in amounts effective to provide control of the fungal disease which is greater than the additive control of that fungal disease provided by the compound(s) of component (1) and the compound(s) of component (2) individually.

Preferred compositions for reasons of ease of synthesis or greater fungicidal activity are:

Preferred 1. A fungicidal composition comprising a fungicidally effective amount of (1) at least one quinazolinone of Formula I (including all geometric and stereoisomers), *N*-oxides, and agriculturally suitable salts thereof, wherein

R¹ is C₁-C₆ alkyl;

R² is C₁-C₆ alkyl;

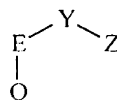
R³ is halogen and fixed at position 6 of the quinazolinone; and

R⁴ is hydrogen or halogen and fixed at position 8 of the quinazolinone;

and (2) at least one compound selected from

5

(a) compounds of Formula II (including all geometric and stereoisomers),
N-oxides, and agriculturally suitable salts thereof,

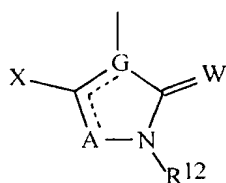


II

5

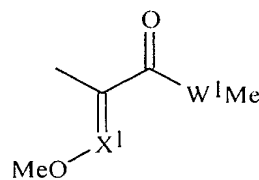
wherein

Q is



Q-1

or



Q-2

10

E is selected from:

15

i) 1,2-phenylene optionally substituted with R^{13} or both R^{13} and R^{14} ;

ii) a naphthalene ring, provided that when G and Y are attached to the same ring, then G and Y are attached to adjacent ring members, the naphthalene ring optionally substituted with R^{13} or both R^{13} and R^{14} ; and

20

iii) a ring system selected from 5 to 12-membered monocyclic and fused bicyclic aromatic heterocyclic ring systems, each heterocyclic ring system containing 1 to 6 heteroatoms independently selected from the group nitrogen, oxygen, and sulfur, provided that each heterocyclic ring system contains no more than 4 nitrogens, no more than 2 oxygens, and no more than 2 sulfurs, each fused bicyclic ring system optionally containing one nonaromatic ring that optionally includes one or two J^1 as ring members and optionally includes one or two ring members independently selected from $C(=O)$ and $S(O)_2$, provided that G is attached to an aromatic ring, and when G and Y are attached to the same ring, then G and Y are attached to adjacent ring members, each aromatic

25

heterocyclic ring system optionally substituted with R^{13} or both R^{13} and R^{14} ;

A is O, S, N, NR^{15} or CR^{24} ;

G is C or N; provided that when G is C, then A is O, S or NR^{15} and the floating double bond is attached to G; and when G is N, then A is N or CR^{24} and the floating double bond is attached to A;

W is O, S, NH, $N(C_1-C_6 \text{ alkyl})$ or $NO(C_1-C_6 \text{ alkyl})$;

W^1 is O or NH;

X is H, OR^{11} , $S(O)_mR^{11}$, halogen, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_3-C_6 cycloalkyl, cyano, NH_2 , NHR^{11} , $N(C_1-C_6 \text{ alkyl})R^{11}$, $NH(C_1-C_6 \text{ alkoxy})$ or $N(C_1-C_6 \text{ alkoxy})R^{11}$;

X^1 is CH or N;

R^{11} is C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_2-C_6 alkenyl, C_2-C_6 haloalkenyl, C_2-C_6 alkynyl, C_2-C_6 haloalkynyl, C_3-C_6 cycloalkyl, C_2-C_4 alkylcarbonyl or C_2-C_4 alkoxycarbonyl;

R^{12} is H, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_2-C_6 alkenyl, C_2-C_6 haloalkenyl, C_2-C_6 alkynyl, C_2-C_6 haloalkynyl, C_3-C_6 cycloalkyl, C_2-C_4 alkylcarbonyl, C_2-C_4 alkoxycarbonyl, hydroxy, C_1-C_2 alkoxy or acetyloxy;

R^{13} and R^{14} are each independently halogen; cyano; nitro; hydroxy; C_1-C_6 alkyl; C_1-C_6 haloalkyl; C_2-C_6 alkenyl; C_2-C_6 haloalkenyl; C_2-C_6 alkynyl; C_2-C_6 haloalkynyl; C_1-C_6 alkoxy; C_1-C_6 haloalkoxy; C_2-C_6 alkenyloxy; C_2-C_6 alkynyloxy; C_1-C_6 alkylthio; C_1-C_6 alkylsulfinyl; C_1-C_6 alkylsulfonyl; formyl; C_2-C_6 alkylcarbonyl; C_2-C_6 alkoxycarbonyl; $NH_2C(O)$; $(C_1-C_4 \text{ alkyl})NHC(O)$; $(C_1-C_4 \text{ alkyl})_2NC(O)$; $Si(R^{35})_3$; $Ge(R^{35})_3$; $(R^{35})_3Si-C\equiv C-$; or phenyl, phenylethynyl, benzoyl, or phenylsulfonyl each substituted with R^{18} and optionally substituted with one or more R^{20} ; or

when E is 1,2-phenylene and R^{13} and R^{14} are attached to adjacent atoms, R^{13} and R^{14} can be taken together as C_3-C_5 alkylene, C_3-C_5 haloalkylene, C_3-C_5 alkenylene or C_3-C_5 haloalkenylene each optionally substituted with 1-2 C_1-C_3 alkyl;

R^{15} is H, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_2-C_6 alkenyl, C_2-C_6 haloalkenyl, C_2-C_6 alkynyl, C_2-C_6 haloalkynyl, C_3-C_6 cycloalkyl, C_2-C_4 alkylcarbonyl or C_2-C_4 alkoxycarbonyl;

Y is $-O-$, $-S(O)_n-$, $-NR^{25}-$, $-C(=O)-$, $-CH(OR^{25})-$, $-CHR^{16}-$, $-CHR^{16}CHR^{16}-$, $-CR^{16}=CR^{16}-$, $-C\equiv C-$, $-CHR^{25}O-$, $-OCHR^{25}-$,

- CHR²⁵S(O)_n-, -S(O)_nCHR²⁵-, -CHR²⁵O-N=C(R¹⁷)-,
 -(R¹⁷)C=N-OCH(R²⁵)-, -C(R¹⁷)=N-O-, -O-N=C(R¹⁷)-,
 -CHR²⁵OC(=O)N(R²⁵)-, -CHR²⁵OC(=S)N(R²⁵)-,
 -CHR²⁵OC(=O)O-, -CHR²⁵OC(=S)O-, -CHR²⁵OC(=O)S-,
 -CHR²⁵OC(=S)S-, -CHR²⁵SC(=O)N(R²⁵)-,
 -CHR²⁵SC(=S)N(R²⁵)-, -CHR²⁵SC(=O)O-, -CHR²⁵SC(=S)O-,
 -CHR²⁵SC(=O)S-, -CHR²⁵SC(=S)S-, -CHR²⁵SC(=NR²⁵)S-,
 -CHR²⁵N(R²⁵)C(=O)N(R²⁵)-, -CHR²⁵O-N(R²⁵)C(=O)N(R²⁵)-,
 -CHR²⁵O-N(R²⁵)C(=S)N(R²⁵)-, -CHR²⁵O-N=C(R¹⁷)NR²⁵-,
 -CHR²⁵O-N=C(R¹⁷)OCH₂-, -CHR²⁵O-N=C(R¹⁷)-N=N-,
 -CHR²⁵O-N=C(R¹⁷)-C(=O)-,
 -CHR²⁵O-N=C(R¹⁷)-C(=N-A²-Z¹)-A¹-,
 -CHR²⁵O-N=C(R¹⁷)-C(R¹⁷)=N-A²-A³-,
 -CHR²⁵O-N=C(-C(R¹⁷)=N-A²-Z¹)-, -CHR²⁵O-N=C(R¹⁷)-CH₂O-,
 -CHR²⁵O-N=C(R¹⁷)-CH₂S-, -O-CH₂CH₂O-N=C(R¹⁷)-,
 -CHR²⁵O-C(R²⁵)=C(R¹⁷)-, -CHR²⁵O-C(R¹⁷)=N-,
 -CHR²⁵S-C(R¹⁷)=N-, -C(R¹⁷)=N-NR²⁵-, -CH=N-N=C(R¹⁷)-,
 -CHR²⁵N(R²⁵)-N=C(R¹⁷)-, -CHR²⁵N(COCH₃)-N=C(R¹⁷)-,
 -OC(=S)NR²⁵C(=O)-, -CHR¹⁶-C(=W²)-A¹-,
 -CHR¹⁶CHR¹⁶-C(=W²)-A¹-, -CR¹⁶=CR¹⁶-C(=W²)-A¹-,
 -C≡C-C(=W²)-A¹-, -N=CR¹⁶-C(=W²)-A¹- or a direct bond; and
 the directionality of the Y linkage is defined such that the moiety
 depicted on the left side of the linkage is bonded to E and the
 moiety on the right side of the linkage is bonded to Z;
- Z¹ is H or -A³-Z;
- W² is O or S;
- A¹ is O, S, NR²⁵ or a direct bond;
- A² is O, NR²⁵ or a direct bond;
- A³ is -C(=O)-, -S(O)₂- or a direct bond;
- each R¹⁶ is independently H, 1-2 CH₃, C₂-C₃ alkyl, C₁-C₃ alkoxy,
 C₃-C₆ cycloalkyl, formylamino, C₂-C₄ alkylcarbonylamino,
 C₂-C₄ alkoxycarbonylamino, NH₂C(O)NH,
 (C₁-C₃ alkyl)NHC(O)NH, (C₁-C₃ alkyl)₂NC(O)NH,
 N(C₁-C₃ alkyl)₂, piperidinyl, morpholinyl, 1-2 halogen, cyano or
 nitro;
- each R¹⁷ is independently H, C₁-C₆ alkyl, C₁-C₆ haloalkyl,
 C₁-C₆ alkoxy, C₁-C₆ haloalkoxy, C₁-C₆ alkylthio,
 C₁-C₆ alkylsulfinyl, C₁-C₆ alkylsulfonyl, C₁-C₆ haloalkylthio,

C₁-C₆ haloalkylsulfinyl, C₁-C₆ haloalkylsulfonyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, C₂-C₆ haloalkynyl, C₃-C₆ cycloalkyl, C₂-C₄ alkylcarbonyl, C₂-C₄ alkoxy carbonyl, halogen, cyano, nitro, hydroxy, amino, NH(C₁-C₆ alkyl),
5 N(C₁-C₆ alkyl)₂ or morpholinyl;

each Z is independently selected from:

i) C₁-C₁₀ alkyl, C₂-C₁₀ alkenyl and C₂-C₁₀ alkynyl each substituted with R¹⁹ and optionally substituted with one or more R²⁰;

10 ii) C₃-C₈ cycloalkyl, C₃-C₈ cycloalkenyl and phenyl each substituted with R¹⁹ and optionally substituted with one or more R²⁰;

15 iii) a ring system selected from 3 to 14-membered monocyclic, fused bicyclic and fused tricyclic nonaromatic heterocyclic ring systems and 5 to 14-membered monocyclic, fused bicyclic and fused tricyclic aromatic heterocyclic ring systems, each heterocyclic ring system containing 1 to 6 heteroatoms independently selected from the group nitrogen, oxygen, and sulfur, provided that each heterocyclic ring system contains no more than 4 nitrogens, no more than 2 oxygens, and no more than 2 sulfurs, each nonaromatic or aromatic heterocyclic ring system substituted with R¹⁹ and optionally substituted with one or more R²⁰;

20 iv) a multicyclic ring system selected from 8 to 14-membered fused-bicyclic and fused-tricyclic ring systems which are an aromatic carbocyclic ring system, a nonaromatic carbocyclic ring system, or a ring system containing one or two nonaromatic rings that each include one or two J¹ as ring members and one or two ring members independently selected from C(=O) and S(O)₂, and any remaining rings as aromatic carbocyclic rings, each multicyclic ring system substituted with R¹⁹ and optionally substituted with one or more R²⁰; and

25 v) adamantyl substituted with R¹⁹ and optionally substituted with one or more R²⁰;

30 each J¹ is independently selected from the group -CHR²³-, -NR²³-, -O- and -S(O)_p-;

R¹⁸ is H, 1-2 halogen, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₁-C₆ alkoxy, C₁-C₆ haloalkoxy, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, C₁-C₆ alkylthio, C₁-C₆ haloalkylthio,

- C₁-C₆ alkylsulfinyl, C₁-C₆ alkylsulfonyl, C₃-C₆ cycloalkyl,
 C₃-C₆ alkenyloxy, CO₂(C₁-C₆ alkyl), NH(C₁-C₆ alkyl),
 N(C₁-C₆ alkyl)₂, cyano, nitro, SiR²⁹R³⁰R³¹ or GeR²⁹R³⁰R³¹;
 R¹⁹ is H; 1-2 halogen; C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₁-C₆ alkoxy;
 5 C₁-C₆ haloalkoxy; C₂-C₆ alkenyl; C₂-C₆ haloalkenyl;
 C₂-C₆ alkynyl; C₁-C₆ alkylthio; C₁-C₆ haloalkylthio;
 C₁-C₆ alkylsulfinyl; C₁-C₆ alkylsulfonyl; C₃-C₆ cycloalkyl;
 C₃-C₆ alkenyloxy; CO₂(C₁-C₆ alkyl); NH(C₁-C₆ alkyl);
 10 N(C₁-C₆ alkyl)₂; -C(R²⁸)=NOR²⁷; cyano; nitro; SF₅;
 SiR³²R³³R³⁴; or GeR³²R³³R³⁴; or R¹⁹ is phenyl, benzyl, benzoyl,
 phenoxy, pyridinyl, pyridinyloxy, thienyl, thienyloxy, furanyl,
 pyrimidinyl or pyrimidinyloxy each optionally substituted with R²¹
 or both R²¹ and R²²;
 each R²⁰ is independently halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl,
 15 C₁-C₄ alkoxy, nitro or cyano; or
 when R¹⁹ and an R²⁰ are attached to adjacent atoms on Z, R¹⁹ and said
 adjacently attached R²⁰ can be taken together as -OCH₂O- or
 -OCH₂CH₂O-; each CH₂ group of said taken together R¹⁹ and R²⁰
 optionally substituted with 1-2 halogen; or
 20 when Y and an R²⁰ are attached to adjacent atoms on Z and Y is
 -CHR²⁵O-N=C(R¹⁷)-, -O-N=C(R¹⁷)-, -O-CH₂CH₂O-N=C(R¹⁷)-,
 -CHR²⁵O-C(R²⁵)=C(R¹⁷)-, -CH=N-N=C(R¹⁷)-,
 -CHR²⁵N(R²⁵)-N=C(R¹⁷)- or -CHR²⁵N(COCH₃)-N=C(R¹⁷)-, R¹⁷
 and said adjacently attached R²⁰ can be taken together as
 25 -(CH₂)_r-J- such that J is attached to Z;
 J is -CH₂-, -CH₂CH₂-, -OCH₂-, -CH₂O-, -SCH₂-, -CH₂S-, -N(R²⁶)CH₂-
 or -CH₂N(R²⁶)-; each CH₂ group of said J optionally substituted
 with 1 to 2 CH₃;
 R²¹ and R²² are each independently 1-2 halogen; C₁-C₄ alkyl;
 30 C₁-C₄ haloalkyl; C₂-C₆ alkenyl; C₂-C₆ haloalkenyl; C₂-C₆
 alkynyl; C₂-C₆ haloalkynyl; C₂-C₆ alkoxyalkyl; C₂-C₆
 alkylthioalkyl; C₃-C₆ alkoxyalkynyl;
 C₇-C₁₀ tetrahydropyranyloxyalkynyl; benzyloxymethyl; C₁-C₄
 alkoxy; C₁-C₄ haloalkoxy; C₃-C₆ alkenyloxy; C₃-C₆
 35 haloalkenyloxy; C₃-C₆ alkynyloxy; C₃-C₆ haloalkynyloxy; C₂-C₆
 alkoxyalkoxy; C₅-C₉ trialkylsilylalkoxyalkoxy;
 C₂-C₆ alkylthioalkoxy; C₁-C₄ alkylthio; C₁-C₄ haloalkylthio;
 C₁-C₄ alkylsulfinyl; C₁-C₄ haloalkylsulfinyl; C₁-C₄ alkylsulfonyl;

- C_1 - C_4 haloalkylsulfonyl; C_3 - C_6 alkenylthio;
 C_3 - C_6 haloalkenylthio; C_2 - C_6 alkylthioalkylthio; nitro; cyano;
 thiocyanato; hydroxy; $N(R^{36})_2$; SF_5 ; $Si(R^{35})_3$; $Ge(R^{35})_3$;
 $(R^{35})_3Si-C\equiv C-$; $OSi(R^{35})_3$; $OGe(R^{35})_3$; $C(=O)R^{36}$; $C(=S)R^{36}$;
 5 $C(=O)OR^{36}$; $C(=S)OR^{36}$; $C(=O)SR^{36}$; $C(=S)SR^{36}$; $C(=O)N(R^{36})_2$;
 $C(=S)N(R^{36})_2$; $OC(=O)R^{36}$; $OC(=S)R^{36}$; $SC(=O)R^{36}$; $SC(=S)R^{36}$;
 $N(R^{36})C(=O)R^{36}$; $N(R^{36})C(=S)R^{36}$; $OC(=O)OR^{37}$; $OC(=O)SR^{37}$;
 $OC(=O)N(R^{36})_2$; $SC(=O)OR^{37}$; $SC(=O)SR^{37}$; $S(O)_2OR^{36}$;
 $S(O)_2N(R^{36})_2$; $OS(O)_2R^{37}$; $N(R^{36})S(O)_2R^{37}$; or phenyl, phenoxy,
 10 benzyl, benzyloxy, phenylsulfonyl, phenylethynyl or
 pyridinylethynyl, each optionally substituted with halogen,
 C_1 - C_4 alkyl, C_1 - C_4 haloalkyl, C_1 - C_4 alkoxy, C_1 - C_4 haloalkoxy,
 nitro or cyano;
 each R^{23} is independently H; C_1 - C_6 alkyl; C_1 - C_6 haloalkyl; or phenyl
 15 optionally substituted with halogen, C_1 - C_4 alkyl, C_1 - C_4 haloalkyl,
 C_1 - C_4 alkoxy, C_1 - C_4 haloalkoxy, nitro or cyano;
 R^{24} is H, halogen, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, C_2 - C_6 alkenyl,
 C_2 - C_6 haloalkenyl, C_2 - C_6 alkynyl, C_2 - C_6 haloalkynyl or
 C_3 - C_6 cycloalkyl;
 20 each R^{25} is independently H; C_1 - C_3 alkyl; C_3 - C_6 cycloalkyl; or phenyl or
 benzyl, each optionally substituted on the phenyl ring with halogen,
 C_1 - C_4 alkyl, C_1 - C_4 haloalkyl, C_1 - C_4 alkoxy, C_1 - C_4 haloalkoxy,
 nitro or cyano; or
 when Y is $-CHR^{25}N(R^{25})C(=O)N(R^{25})-$, the two R^{25} attached to
 25 nitrogen atoms on said group can be taken together as $-(CH_2)_s-$; or
 when Y is $-CHR^{25}O-N=C(R^{17})NR^{25}-$, R^{17} and the adjacently attached
 R^{25} can be taken together as $-CH_2-(CH_2)_s-$, $-O-(CH_2)_s-$,
 $-S-(CH_2)_s-$ or $-N(C_1-C_3 \text{ alkyl})-(CH_2)_s-$; with the directionality of
 said linkage defined such that the moiety depicted on the left side
 30 of the linkage is bonded to the carbon and the moiety on the right
 side of the linkage is bonded to the nitrogen;
 R^{26} , R^{27} and R^{28} are each independently H; C_1 - C_3 alkyl;
 C_3 - C_6 cycloalkyl; or phenyl optionally substituted with halogen,
 C_1 - C_4 alkyl, C_1 - C_4 haloalkyl, C_1 - C_4 alkoxy, C_1 - C_4 haloalkoxy,
 35 nitro or cyano;
 R^{29} , R^{30} , R^{31} , R^{32} , R^{33} and R^{34} are each independently C_1 - C_6 alkyl,
 C_2 - C_6 alkenyl, C_1 - C_4 alkoxy or phenyl;

each R³⁵ is independently C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₂-C₄ alkenyl, C₁-C₄ alkoxy or phenyl;

each R³⁶ is independently H; C₁-C₆ alkyl; C₁-C₆ haloalkyl;

C₂-C₆ alkenyl; C₂-C₆ haloalkenyl; C₂-C₆ alkynyl;

5 C₂-C₆ haloalkynyl; C₃-C₆ cycloalkyl; or phenyl or benzyl, each optionally substituted on the phenyl ring with halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, nitro or cyano;

each R³⁷ is independently C₁-C₆ alkyl; C₁-C₆ haloalkyl; C₂-C₆ alkenyl; C₂-C₆ haloalkenyl; C₂-C₆ alkynyl; C₂-C₆ haloalkynyl;

10 C₃-C₆ cycloalkyl; or phenyl or benzyl, each optionally substituted on the phenyl ring with halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, nitro or cyano;

m, n and p are each independently 0, 1 or 2;

r is 0 or 1; and

15 s is 2 or 3;

and (b) bromuconazole, cyproconazole, difenoconazole, diniconazole, epoxiconazole, fenarimol, fenbuconazole, fenpropidin, fenpropimorph, fluquinconazole, flusilazole, flutriafol, hexaconazole, ipconazole, metconazole, penconazole, propiconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, tridemorph, triticonazole and uniconazole.

Preferred 2. The fungicidal composition of Preferred 1 comprising a fungicidally effective amount of (1) at least one compound selected from the group consisting of

25 6-bromo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone, 6,8-diiodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone and 6-iodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone;

and (2) at least one compound selected from the group consisting of

30 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3*H*-1,2,4-triazol-3-one, kresoxim-methyl, azoxystrobin, (*E*)-2-(methoxyimino)-*N*-methyl-2-(2-phenoxyphenyl)acetamide, flusilazole, epoxiconazole, fenpropimorph, propiconazole and tebuconazole.

35 Preferred 3. The fungicidal composition of Preferred 2 comprising a fungicidally effective amount of (1) 6-iodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone (sometimes referred to hereafter as the Formula Ia compound) and (2) 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-

(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3*H*-1,2,4-triazol-3-one (sometimes referred to hereafter as the Formula IIa compound).

5 Preferred 4. The fungicidal composition of Preferred 2 comprising a fungicidally effective amount of (1) 6-iodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone and (2) flusilazole.

Preferred 5. The fungicidal composition of Preferred 2 comprising a fungicidally effective amount of (1) 6-iodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone and (2) tebuconazole.

10 Preferred 6. The fungicidal composition of Preferred 2 comprising a fungicidally effective amount of (1) 6-iodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone, and (2) both 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3*H*-1,2,4-triazol-3-one and flusilazole.

15 In the above recitations, the term "alkyl", used either alone or in compound words such as "alkylthio" or "haloalkyl" includes straight-chain or branched alkyl, such as, methyl, ethyl, *n*-propyl, *i*-propyl, or the different butyl, pentyl, hexyl, heptyl, octyl, nonyl and decyl isomers. The term "1-2 CH₃" indicates that the substituent can be methyl (i.e., Me) or, when there is a hydrogen attached to the same atom, the substituent
20 and said hydrogen can both be methyl. "Alkenyl" includes straight-chain or branched alkenes such as ethenyl, 1-propenyl, 2-propenyl, and the different butenyl, pentenyl, hexenyl, heptenyl, octenyl, nonenyl and decenyl isomers. "Alkenyl" also includes polyenes such as 1,2-propadienyl and 2,4-hexadienyl. "Alkynyl" includes straight-chain or branched alkynes such as ethynyl, 1-propynyl, 2-propynyl and the different butynyl, pentynyl, hexynyl, heptynyl, octynyl, nonynyl, and decynyl isomers. "Alkynyl" can
25 also include moieties comprised of multiple triple bonds such as 2,5-hexadiynyl.

"Alkylene" denotes a straight-chain or branched alkanediyl. Examples of "alkylene" include CH₂CH₂CH₂, CH₂CH(CH₃) and the different butylene and pentylene isomers. "Haloalkylene" denotes a halogen substituted alkylene. Examples
30 of "haloalkylene" include CH₂CH(CF₃), CH₂CF₂CH₂ and CH₂CH(CCl₃). "Alkenylene" denotes a straight-chain or branched alkenediyl containing one olefinic bond. Examples of "alkenylene" include CH₂CH=CH and CH=C(CH₃) and the different butenylene and pentenylene isomers. "Haloalkenylene" denotes a halogen substituted alkenylene. Examples of "haloalkenylene" include CH₂CCl=CCl and
35 CH=C(CF₃).

"Alkenyloxyalkyl" denotes alkenyl substitution on oxygen which in turn is substituted on alkyl. Examples "alkenyloxyalkyl" include CH₂=CHCH₂OCH₂ and CH₃CH=CHCH₂OCH₂CH₂. "Alkynyloxyalkyl" denotes alkynyl substitution on

oxygen which in turn is substituted on alkyl. Examples of "alkynyloxyalkyl" include $\text{CH}\equiv\text{CCH}_2\text{OCH}_2$ and $\text{CH}_3\text{C}\equiv\text{CCH}_2\text{OCH}_2\text{CH}_2$.

- "Alkoxy" includes, for example, methoxy, ethoxy, propyloxy, 1-methylethoxy and the different butoxy, pentyloxy, hexyloxy, heptyloxy, octyloxy, nonyloxy, and decyloxy isomers. "Alkoxyalkyl" denotes alkoxy substitution on alkyl. Examples of "alkoxyalkyl" include CH_3OCH_2 , $\text{CH}_3\text{OCH}_2\text{CH}_2$, $\text{CH}_3\text{CH}_2\text{OCH}_2$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_2$ and $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2$. "Alkoxyalkoxy" denotes alkoxy substitution on alkoxy. Examples of "alkoxyalkoxy" include $\text{CH}_3\text{OCH}_2\text{O}$, $(\text{CH}_3)_3\text{COCH}_2\text{O}$ and $\text{CH}_3\text{OCH}_2\text{CH}_2\text{O}$. "Alkenyloxy" includes straight-chain or branched alkenyloxy moieties. Examples of "alkenyloxy" include $\text{H}_2\text{C}=\text{CHCH}_2\text{O}$, $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{O}$, $(\text{CH}_3)\text{CH}=\text{CHCH}_2\text{O}$, $(\text{CH}_3)\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2\text{O}$ and $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{O}$. "Alkynyloxy" includes straight-chain or branched alkynyloxy moieties. Examples of "alkynyloxy" include $\text{HC}\equiv\text{CCH}_2\text{O}$, $\text{CH}_3\text{C}\equiv\text{CCH}_2\text{O}$ and $\text{CH}_3\text{C}\equiv\text{CCH}_2\text{CH}_2\text{O}$. "Alkoxyalkenyl" denotes alkoxy substitution of alkenyl.
- "Alkoxyalkenyl" includes straight-chain or branched alkoxyalkenyl moieties. Examples of "alkoxyalkenyl" include $(\text{CH}_3)_2\text{CHOCH}=\text{CH}$ and $\text{CH}_3\text{OCH}_2\text{CH}=\text{CH}$. "Alkoxyalkynyl" denotes alkoxy substitution of alkynyl. "Alkoxyalkynyl" includes straight-chain or branched alkoxyalkynyl moieties. Examples of "alkoxyalkynyl" include $(\text{CH}_3)_2\text{CHOCH}_2\text{C}\equiv\text{C}$ and $\text{CH}_3\text{OCH}_2\text{C}\equiv\text{C}$.
- "Alkylthio" includes branched or straight-chain alkylthio moieties such as methylthio, ethylthio, and the different propylthio, butylthio, pentylthio, hexylthio, heptylthio, octylthio, nonylthio and decylthio isomers. "Alkylthioalkyl" denotes alkylthio substitution on alkyl. Examples of "alkylthioalkyl" include CH_3SCH_2 , $\text{CH}_3\text{SCH}_2\text{CH}_2$, $\text{CH}_3\text{CH}_2\text{SCH}_2$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{SCH}_2$ and $\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_2$.
- "Alkylthioalkoxy" denotes alkylthio substitution on alkoxy. Examples of "alkylthioalkoxy" include $\text{CH}_3\text{SCH}_2\text{O}$ and $\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_2\text{O}$. "Alkylthioalkylthio" denotes alkylthio substitution on alkylthio. Examples of "alkylthioalkylthio" include $\text{CH}_3\text{SCH}_2\text{S}$ and $\text{CH}_3\text{SCH}_2\text{CH}_2\text{S}$. "Alkylsulfinyl" includes both enantiomers of an alkylsulfinyl group. Examples of "alkylsulfinyl" include $\text{CH}_3\text{S}(\text{O})$, $\text{CH}_3\text{CH}_2\text{S}(\text{O})$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{S}(\text{O})$, $(\text{CH}_3)_2\text{CHS}(\text{O})$ and the different butylsulfinyl, pentylsulfinyl, hexylsulfinyl, heptylsulfinyl and octylsulfinyl isomers. "Alkylsulfinylalkyl" denotes alkylsulfinyl substitution on alkyl. Examples of "alkylsulfinylalkyl" include $\text{CH}_3\text{S}(\text{O})\text{CH}_2$, $\text{CH}_3\text{S}(\text{O})\text{CH}_2\text{CH}_2$, $\text{CH}_3\text{CH}_2\text{S}(\text{O})\text{CH}_2$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{S}(\text{O})\text{CH}_2$ and $\text{CH}_3\text{CH}_2\text{S}(\text{O})\text{CH}_2\text{CH}_2$. Examples of "alkylsulfonyl" include $\text{CH}_3\text{S}(\text{O})_2$, $\text{CH}_3\text{CH}_2\text{S}(\text{O})_2$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{S}(\text{O})_2$, $(\text{CH}_3)_2\text{CHS}(\text{O})_2$ and the different butylsulfonyl, pentylsulfonyl, hexylsulfonyl, heptylsulfonyl and octylsulfonyl isomers.
- "Alkylsulfonylalkyl" denotes alkylsulfonyl substitution on alkyl. Examples of "alkylsulfonylalkyl" include $\text{CH}_3\text{S}(\text{O})_2\text{CH}_2$, $\text{CH}_3\text{S}(\text{O})_2\text{CH}_2\text{CH}_2$, $\text{CH}_3\text{CH}_2\text{S}(\text{O})_2\text{CH}_2$,

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{S}(\text{O})_2\text{CH}_2$ and $\text{CH}_3\text{CH}_2\text{S}(\text{O})_2\text{CH}_2\text{CH}_2$. "Alkylthioalkenyl" denotes alkylthio substitution on alkenyl. Examples of "alkylthioalkenyl" include $\text{CH}_3\text{SCH}_2\text{CH}=\text{CH}$ and $\text{CH}_3\text{CH}_2\text{SCH}=\text{CH}$. "Alkylthioalkynyl" denotes alkylthio substitution on alkynyl. Examples of "alkylthioalkynyl" include $\text{CH}_3\text{SCH}_2\text{C}\equiv\text{C}$ and $\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_2\text{C}\equiv\text{C}$. "Alkenylthio" includes straight-chain and branched alkenylthio moieties. Examples of "alkenylthio" include $\text{CH}_2=\text{CHCH}_2\text{S}$ and $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{S}$. "Alkenylthioalkyl" denotes alkenylthio substitution on alkyl. Examples of "alkenylthioalkyl" include $\text{CH}_2=\text{CHCH}_2\text{SCH}_2$ and $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{SCH}_2$. "Alkynylthio" includes straight-chain and branched alkynylthio moieties. Examples of "alkynylthio" include $\text{CH}\equiv\text{CCH}_2\text{S}$ and $\text{CH}\equiv\text{CCH}_2\text{CH}_2\text{S}$. "Alkynylthioalkyl" denotes alkynylthio substitution on alkyl. Examples of "alkynylthioalkyl" include $\text{CH}\equiv\text{CCH}_2\text{SCH}_2$ and $\text{CH}\equiv\text{CCH}_2\text{CH}_2\text{SCH}_2$.

"Cycloalkyl" includes, for example, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl and cyclooctyl. "(Cycloalkyl)oxyalkyl" denotes cycloalkyl substituted on oxygen which in turn is substituted on alkyl. Examples of "(cycloalkyl)oxyalkyl" include (cyclopentyloxy)methyl and (cyclohexyloxy)methyl. "(Cycloalkyl)thioalkyl" denotes cycloalkyl substituted on sulfur which in turn is substituted on alkyl. Examples of "(cycloalkyl)thioalkyl" include (cyclopentylthio)methyl and (cyclohexylthio)methyl. "Cycloalkenyl" includes groups such as cyclopentenyl and cyclohexenyl as well as groups with more than one double bond such as 1,3- and 1,4-cyclohexadienyl. Examples of "cycloalkylalkyl" include cyclopropylmethyl, cyclopentylethyl, and other cycloalkyl moieties bonded to straight-chain or branched alkyl groups.

"Cyanoalkyl" denotes an alkyl group substituted with one cyano group. Examples of "cyanoalkyl" include NCCH_2 , NCCH_2CH_2 and $\text{CH}_3\text{CH}(\text{CN})\text{CH}_2$. "Nitroalkyl" denotes an alkyl group substituted with one nitro group. Examples of "nitroalkyl" include NO_2CH_2 and $\text{CH}_3\text{CH}(\text{NO}_2)\text{CH}_2$.

"Tetrahydropyranyloxyalkynyl" denotes a tetrahydropyranyl group on oxygen which in turn is substituted on an alkynyl group. An example of "tetrahydropyranyloxyalkynyl" is 2-[(tetrahydro-2*H*-pyranyl)oxy]ethynyl.

The term "aromatic ring system" denotes fully unsaturated carbocycles and heterocycles in which the polycyclic ring system is aromatic (where aromatic indicates that the Hückel rule is satisfied for the ring system). The term "aromatic carbocyclic ring system" includes fully aromatic carbocycles and carbocycles in which at least one ring of a polycyclic ring system is aromatic (where aromatic indicates that the Hückel rule is satisfied). The term "nonaromatic carbocyclic ring system" denotes fully saturated carbocycles as well as partially or fully unsaturated carbocycles where the Hückel rule is not satisfied by any of the rings in the ring system. The term "aromatic

heterocyclic ring system" includes fully aromatic heterocycles and heterocycles in which at least one ring of a polycyclic ring system is aromatic (where aromatic indicates that the Hückel rule is satisfied). Examples of "aromatic heterocyclic ring systems" include furanyl, furazanyl, thienyl, pyrrolyl, pyrazolyl, oxazolyl, oxadiazolyl, 5 imidazolyl, isoxazolyl, thiazolyl, thiadiazolyl, isothiazolyl, pyridyl, pyrimidinyl, pyridazinyl, pyrazinyl and triazinyl with said ring attached through any available carbon or nitrogen. For example, when the aromatic heterocyclic ring is furanyl, it can be 2-furanyl or 3-furanyl, for pyrrolyl, the aromatic heterocyclic ring is 1-pyrrolyl, 2-pyrrolyl or 3-pyrrolyl, for pyridyl, the aromatic ring is 2-pyridyl, 3-pyridyl or 10 4-pyridyl and similarly for other aromatic heterocyclic rings. The term "nonaromatic heterocyclic ring system" denotes fully saturated heterocycles as well as partially or fully unsaturated heterocycles where the Hückel rule is not satisfied by any of the rings in the ring system. The heterocyclic ring systems can be attached through any available carbon or nitrogen by replacement of a hydrogen on said carbon or nitrogen.

15 One skilled in the art will appreciate that not all nitrogen containing heterocycles can form *N*-oxides since the nitrogen requires an available lone pair for oxidation to the oxide; one skilled in the art will recognize those nitrogen containing heterocycles which can form *N*-oxides. One skilled in the art will also recognize that tertiary amines can form *N*-oxides. Synthetic methods for the preparation of *N*-oxides of heterocycles and 20 tertiary amines are very well known by one skilled in the art including the oxidation of heterocycles and tertiary amines with peroxy acids such as peracetic and *m*-chloroperbenzoic acid (MCPBA), hydrogen peroxide, alkyl hydroperoxides such as *t*-butyl hydroperoxide, sodium perborate, and dioxiranes such as dimethyldioxirane. These methods for the preparation of *N*-oxides have been extensively described and 25 reviewed in the literature, see for example: T. L. Gilchrist in *Comprehensive Organic Synthesis*, vol. 7, pp 748-750, S. V. Ley, Ed., Pergamon Press; M. Tisler and B. Stanovnik in *Comprehensive Heterocyclic Chemistry*, vol. 3, pp 18-20, A. J. Boulton and A. McKillop, Eds., Pergamon Press; M. R. Grimmett and B. R. T. Keene in *Advances in Heterocyclic Chemistry*, vol. 43, pp 149-161, A. R. Katritzky, Ed., 30 Academic Press; M. Tisler and B. Stanovnik in *Advances in Heterocyclic Chemistry*, vol. 9, pp 285-291, A. R. Katritzky and A. J. Boulton, Eds., Academic Press; and G. W. H. Cheeseman and E. S. G. Werstiuk in *Advances in Heterocyclic Chemistry*, vol. 22, pp 390-392, A. R. Katritzky and A. J. Boulton, Eds., Academic Press.

35 The term "halogen", either alone or in compound words such as "haloalkyl", includes fluorine, chlorine, bromine or iodine. The term "1-2 halogen" indicates that one or two of the available positions for that substituent may be halogen which are independently selected. Further, when used in compound words such as "haloalkyl", said alkyl may be partially or fully substituted with halogen atoms which may be the

- same or different. Examples of "haloalkyl" include F_3C , $ClCH_2$, CF_3CH_2 and CF_3CCl_2 . The terms "haloalkenyl", "haloalkenyloxy", "haloalkenylthio", "haloalkenyloxyalkyl", "haloalkynyl", "haloalkynyloxy", "haloalkynyloxyalkyl", "haloalkoxy", "haloalkoxyalkyl", "haloalkylthio", "haloalkylsulfinyl",
- 5 "haloalkylsulfonyl", and the like, are defined analogously to the term "haloalkyl". Examples of "haloalkenyl" include $(Cl)_2C=CHCH_2$ and $CF_3CH_2CH=CHCH_2$. Examples of "haloalkenyloxy" include $(Cl)_2C=CHCH_2O$ and $CF_3CH_2CH=CHCH_2O$. Examples of "haloalkenylthio" include $(Cl)_2C=CHCH_2S$ and $CF_3CH_2CH=CHCH_2S$. Examples of "haloalkenyloxyalkyl" include $(Cl)_2C=CHCH_2OCH_2$ and
- 10 $CF_3CH_2CH=CHCH_2OCH_2$. Examples of "haloalkynyl" include $HC\equiv CCHCl$, $CF_3C\equiv C$, $CCl_3C\equiv C$ and $FCH_2C\equiv CCH_2$. Examples of "haloalkynyloxy" include $CF_3C\equiv CCH_2O$, $CCl_3C\equiv CCH_2O$ and $FCH_2C\equiv CCH_2O$. Examples of "haloalkynyloxyalkyl" include $CCl_3C\equiv CCH_2OCH_2$ and $FCH_2C\equiv CCH_2CH_2OCH_2$. Examples of "haloalkoxy" include CF_3O , CCl_3CH_2O , $HCF_2CH_2CH_2O$ and CF_3CH_2O . Examples of "haloalkoxyalkyl"
- 15 include CF_3OCH_2 , $CCl_3CH_2OCH_2CH_2$, $HCF_2CH_2CH_2OCH_2$ and $CF_3CH_2OCH_2$. Examples of "haloalkylthio" include CCl_3S , CF_3S , CCl_3CH_2S and $ClCH_2CH_2CH_2S$. Examples of "haloalkylsulfinyl" include $CF_3S(O)$, $CCl_3S(O)$, $CF_3CH_2S(O)$ and $CF_3CF_2S(O)$. Examples of "haloalkylsulfonyl" include $CF_3S(O)_2$, $CCl_3S(O)_2$, $CF_3CH_2S(O)_2$ and $CF_3CF_2S(O)_2$.
- 20 "Alkylcarbonyl" denotes alkyl substituted carbonyl. Examples of "alkylcarbonyl" include $CH_3C(=O)$ and $(CH_3)_2CHC(=O)$. "Alkoxycarbonyl" denotes alkoxy substituted carbonyl. Examples of "alkoxycarbonyl" include $CH_3OC(=O)$ and $(CH_3)_2CHOC(=O)$. "Alkylcarbonylamino" denotes alkylcarbonyl substituted on nitrogen. Examples of "alkylcarbonylamino" include $CH_3C(=O)NH$ and $CH_3CH_2C(=O)NH$.
- 25 "Alkoxycarbonylamino" denotes alkoxycarbonyl substituted on nitrogen. Examples of "alkoxycarbonylamino" include $CH_3OC(=O)NH$ and $CH_3CH_2OC(=O)NH$.
- Examples of "trialkylsilyl" include $(CH_3)_3Si$ and $(CH_3)_3CSi(CH_3)_2$. "Trialkylsilylalkyl" denotes trialkylsilyl substitution on alkyl. Examples of "trialkylsilylalkyl" include $(CH_3)_3SiCH_2$, and $(CH_3)_3SiCH_2CH_2$.
- 30 "Trialkylsilylalkynyl" denotes trialkylsilyl substitution on alkynyl. Examples of "trialkylsilylalkynyl" include $(CH_3)_3SiC\equiv C$ and $(CH_3CH_2)_3SiCH_2C\equiv C$. "Trialkylsilylalkoxyalkoxy" denotes trialkylsilyl substitution on alkoxy substituted in turn on alkoxy. Examples of "trialkylsilylalkoxyalkoxy" include $(CH_3)_3SiCH_2OCH_2O$ and $(CH_3)_3SiCH_2CH_2OCH_2O$.
- 35 The total number of carbon atoms in a substituent group is indicated by the " C_i-C_j " prefix where i and j are numbers from 1 to 11. For example, C_1-C_3 alkylsulfonyl designates methylsulfonyl through propylsulfonyl; C_2 alkoxyalkyl designates CH_3OCH_2 ; C_3 alkoxyalkyl designates, for example, $CH_3CH(OCH_3)$,

$\text{CH}_3\text{OCH}_2\text{CH}_2$ or $\text{CH}_3\text{CH}_2\text{OCH}_2$; and C_4 alkoxyalkyl designates the various isomers of an alkyl group substituted with an alkoxy group containing a total of four carbon atoms, examples including $\text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_2$ and $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2$. Examples of "alkylcarbonyl" include $\text{C}(\text{O})\text{CH}_3$, $\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{C}(\text{O})\text{CH}(\text{CH}_3)_2$. Examples of "alkoxycarbonyl" include $\text{CH}_3\text{OC}(=\text{O})$, $\text{CH}_3\text{CH}_2\text{OC}(=\text{O})$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OC}(=\text{O})$, $(\text{CH}_3)_2\text{CHOC}(=\text{O})$ and the different butoxy- or pentoxycarbonyl isomers. In the above recitations, when a compound of Formula I is comprised of one or more heterocyclic rings, all substituents are attached to these rings through any available carbon or nitrogen by replacement of a hydrogen on said carbon or nitrogen.

10 When a compound is substituted with a substituent bearing a subscript that indicates the number of said substituents can exceed 1, said substituents (when they exceed 1) are independently selected from the group of defined substituents. Further, when the subscript indicates a range, e.g., $(\text{R})_{i-j}$, then the number of substituents may be selected from the integers between i and j inclusive.

15 When a group contains a substituent which can be hydrogen, for example R^4 , then, when this substituent is taken as hydrogen, it is recognized that this is equivalent to said group being unsubstituted. When a group is optionally substituted with a substituent, for example with R^7 , then, when the group is not substituted with that substituent, it is recognized that this is equivalent to said group having a hydrogen substituent.

20 Compounds used in this invention often can exist as one or more stereoisomers. The various stereoisomers include enantiomers, diastereomers, atropisomers and geometric isomers. One skilled in the art will appreciate that one stereoisomer may be more active and/or may exhibit beneficial effects when enriched relative to the other stereoisomer(s) or when separated from the other stereoisomer(s). (See, e.g., U.S. Provisional Patent Application Serial No. 60/057917 filed September 4, 1997, which is hereby incorporated by reference in its entirety.) Additionally, the skilled artisan knows how to separate, enrich, and/or to selectively prepare said stereoisomers. Accordingly, the present invention comprises compounds selected from Formula I, *N*-oxides and agriculturally suitable salts thereof. The compounds of the invention may be present as a mixture of stereoisomers, individual stereoisomers, or as an optically active form.

30 The salts of the compounds which may be used in the invention include acid-addition salts with inorganic or organic acids such as hydrobromic, hydrochloric, nitric, phosphoric, sulfuric, acetic, butyric, fumaric, lactic, maleic, malonic, oxalic, propionic, salicylic, tartaric, 4-toluenesulfonic or valeric acids. The salts of the compounds which may be used in the invention also include those formed with organic bases (e.g., pyridine, ammonia, or triethylamine) or inorganic bases (e.g., hydrides, hydroxides, or

carbonates of sodium, potassium, lithium, calcium, magnesium or barium) when the compound contains an acidic group such as a carboxylic acid or phenol.

The fungicidal compositions of this invention, in addition to comprising fungicidally effective amounts of the mixtures of the invention, also optionally comprise at least one of a surfactant, a solid diluent or a liquid diluent. The preferred compositions of the present invention are those which comprise the above preferred component (1) and component (2) compounds.

This invention also relates to a method for controlling plant diseases caused by fungal plant pathogens comprising applying to the plant or portion thereof, or to the plant seed or seedling, a fungicidally effective amount of the compositions of the invention (e.g., as a composition described herein). The preferred methods of use include those involving the above preferred compositions.

The bc_1 Complex Fungicides

Compounds of Formula II are known to have a fungicidal mode of action which inhibits the bc_1 complex. Methyl (*E*)-2-[[6-(2-cyanophenoxy)-4-pyrimidinyl]oxy]- α -(methoxyimino)benzeneacetate is described as a bc_1 complex inhibitor in *Biochemical Society Transactions* 1993, 22, 68S. Methyl (*E*)- α -(methoxyimino)-2-[(2-methylphenoxy)methyl]benzeneacetate is described as a bc_1 complex inhibitor in *Biochemical Society Transactions* 1993, 22, 64S. (*E*)-2-[(2,5-Dimethylphenoxy)methyl]- α -(methoxyimino)-*N*-methylbenzeneacetamide is described as a bc_1 complex inhibitor in *Biochemistry and Cell Biology* 1995, 85(3), 306-311.

The bc_1 complex is sometimes referred to by other names in the biochemical literature, including complex III of the electron transfer chain, and ubiquinone:cytochrome c oxidoreductase. It is uniquely identified by the Enzyme Commission number EC1.10.2.2. The bc_1 complex is described in, for example, *J. Biol. Chem.* 1989, 264, 14543-38; *Methods Enzymol.* 1986, 126, 253-71; and references cited therein.

The Sterol Biosynthesis Inhibitor Fungicides

The class of sterol biosynthesis inhibitors includes DMI and non-DMI compounds, that control fungi by inhibiting enzymes in the sterol biosynthesis pathway. DMI fungicides have a common site of action within the fungal sterol biosynthesis pathway; that is, an inhibition of demethylation at position 14 of lanosterol or 24-methylene dihydrolanosterol, which are precursors to sterols in fungi. Compounds acting at this site are often referred to as demethylase inhibitors, DMI fungicides, or DMIs. The demethylase enzyme is sometimes referred to by other names in the biochemical literature, including cytochrome P-450 (14DM). The demethylase enzyme is described in, for example, *J. Biol. Chem.* 1992, 267, 13175-79 and references cited therein. DMI fungicides fall into several classes: triazoles, imidazoles, pyrimidines,

piperazines and pyridines. The triazoles includes bromuconazole, cyproconazole, difenoconazole, diniconazole, epoxiconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, hexaconazole, ipconazole, metconazole, penconazole, propiconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triticonazole and uniconazole. The imidazoles include clotrimazole, econazole, imazalil, isoconazole, miconazole and prochloraz. The pyrimidines include fenarimol, nuarimol and triarimol. The piperazines include triforine. The pyridines include buthiobate and pyrifenoxy. Biochemical investigations have shown that all of the above mentioned fungicides are DMI fungicides as described by K. H. Kuck, et al. in *Modern Selective Fungicides - Properties, Applications and Mechanisms of Action*, Lyr, H., Ed.; Gustav Fischer Verlag: New York, 1995, 205-258.

The DMI fungicides have been grouped together to distinguish them from other sterol biosynthesis inhibitors, such as, the morpholine and piperidine fungicides. The morpholines and piperidines are also sterol biosynthesis inhibitors but have been shown to inhibit later steps in the sterol biosynthesis pathway. The morpholines include aldimorph, dodemorph, fenpropimorph, tridemorph and trimorphamide. The piperidines include fenpropidin. Biochemical investigations have shown that all of the above mentioned morpholine and piperidine fungicides are sterol biosynthesis inhibitor fungicides as described by K. H. Kuck, et al. in *Modern Selective Fungicides - Properties, Applications and Mechanisms of Action*, Lyr, H., Ed.; Gustav Fischer Verlag: New York, 1995, 185-204.

Synergistic Effects

Fungicides that effectively control plant fungi, particularly wheat powdery mildew (*Erysiphe graminis*) and wheat foot rot (*Pseudocercospora herpotrichoides*), are in constant demand by growers. Combinations of fungicides are often used to facilitate disease control and to retard resistance development. Mixtures of fungicides may provide significantly better disease control than could be predicted based on the activity of the individual components. This synergism has been described as "the cooperative action of two components of a mixture, such that the total effect is greater or more prolonged than the sum of the effects of the two (or more) taken independently" (see Tames, P. M. L., *Neth. J. Plant Pathology*, (1964), 70, 73-80). It has been demonstrated that compositions containing compounds of Formula Ia and Formula IIa; Formula Ia and flusilazole; Formula Ia and tebuconazole; and Formula Ia, Formula IIa and flusilazole exhibit synergistic effects.

The presence of a synergistic effect between two active ingredients is established with the aid of the Colby equation (see Colby, S. R. In *Calculating Synergistic and Antagonistic Responses of Herbicide Combinations*, Weeds, (1967), 15, 20-22):

20

$$p = A + B - \left[\frac{A \times B}{100} \right]$$

Using the methods of the Colby, the presence of a synergistic interaction between two active ingredients is established by first calculating the predicted activity, p , of the mixture based on activities of the two components applied alone. If p is lower than the experimentally established effect, synergism has occurred. In the equation above, A is the fungicidal activity in percentage control of one component applied alone at rate x . The B term is the fungicidal activity in percentage control of the second component applied at rate y . The equation estimates p , the fungicidal activity of the mixture of A at rate x with B at rate y if their effects are strictly additive and no interaction has occurred.

The Colby equation for a three way mixture is

$$p = A + B + C + \frac{A \times B \times C}{10000} - \left[\frac{(A \times B) + (A \times C) + (B \times C)}{100} \right]$$

In this application, fungicidal activities provided by compositions of Formula Ia, Formula IIa, flusilazole and tebuconazole alone are compared with that of compositions of the compounds of Formula Ia and Formula IIa together, compositions of the compounds of Formula Ia and flusilazole together, compositions of the compounds of Formula Ia and tebuconazole together, and compositions of the compounds of Formula Ia, Formula IIa and flusilazole together. Based on the description of synergism developed by Colby, compositions of the present invention are considered to be synergistically useful. Accordingly, this invention provides an improved method of combating fungi, such as wheat powdery mildew (*Erysiphe graminis*), wheat leaf rust (*Puccinia recondita*), wheat foot rot (*Pseudocercospora herpotrichoides*) and/or wheat glume blotch (*Septoria nodorum*) in crops, especially cereals.

Compositions are provided in accordance with this invention which comprise proportions of component (1) and component (2) which are especially useful for controlling particular fungal diseases. For example, the compositions of this invention include those wherein the mole ratio of component (1) to component (2) is from about 30:1 to 1:30. These compositions are considered especially useful for controlling wheat powdery mildew (*Erysiphe graminis*), wheat leaf rust (*Puccinia recondita*), wheat foot rot (*Pseudocercospora herpotrichoides*) and/or wheat glume blotch (*Septoria nodorum*). Preferred component (1) compounds for these compositions include 6-bromo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone; 6,8-diiodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone; and 6-iodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone; with 6-iodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone being particularly preferred.

Preferred component (2) compounds for these compositions include 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-

(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3*H*-1,2,4-triazol-3-one, kresoxim-methyl, azoxystrobin, (*E*)-2-(methoxyimino)-*N*-methyl-2-(2-

5 phenoxyphenyl)acetamide, flusilazole, epoxiconazole, fenpropimorph, propiconazole and tebuconazole; with 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3*H*-1,2,4-triazol-3-one, fenpropimorph, flusilazole, epoxiconazole and propiconazole being particularly preferred. Preferably, the mole ratio of component (1) to component (2) for these

10 compositions is from about 4:1 to 1:4. Example compositions of this type include compositions comprising 6-iodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone and 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-

(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3*H*-1,2,4-triazol-3-one in a mole ratio of the compound of Formula Ia to the compound of Formula IIa of from about 4:1 to 1:4, compositions comprising

15 6-iodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone and fenpropimorph in a mole ratio of the compound of Formula Ia to fenpropimorph of from about 1:1 to 1:10, compositions comprising 6-iodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone and flusilazole in a mole ratio of the compound of Formula Ia to flusilazole of from about 15:1 to 1:15,

20 compositions comprising 6-iodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone and tebuconazole in a mole ratio of the compound of Formula Ia to tebuconazole of from about 30:1 to 1:30, and compositions comprising

6-iodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone; 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3*H*-1,2,4-triazol-3-one; and flusilazole in a mole ratio of the compound of Formula Ia to the compound of Formula IIa plus flusilazole of from about 4:1 to 1:4 and the compound of Formula IIa to flusilazole has a mole ratio of from about 4:1 to 1:4.

This invention also provides a process for controlling at least one plant disease selected from wheat powdery mildew, wheat leaf rust, wheat foot rot, and wheat glume blotch which comprises applying to the plant or portion thereof to be protected, or to the plant seed or seedling to be protected, an effective amount of a fungicidal combination including component (1) and component (2) wherein the mole ratio of component (1) to component (2) is from about 30:1 to 1:30 (preferably from about 4:1 to 1:4).

Component (1) can, for example, be applied at a rate of 0.2 g/ha or more. Typically component (1) is applied at a rate of 100 g/ha. Component (2) may be applied simultaneously (e.g., in the form of a composition comprising component (1) and component (2) in an appropriate mole ratio); or component (1) and component (2) can be applied separately in an appropriate mole ratio (e.g., as a tank mix).

Compositions wherein component (2) is selected from the group consisting of 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3*H*-1,2,4-triazol-3-one, kresoxim-methyl, azoxystrobin, (*E*)-2-(methoxyimino)-*N*-methyl-2-(2-phenoxyphenyl)acetamide, flusilazole, epoxiconazole, fenpropimorph, propiconazole and tebuconazole; and wherein the mole ratio of component (1) to component (2) is from about 4:1 to 1:10 are considered especially useful for controlling wheat powdery mildew. Preferred component (1) compounds for these compositions include

6-bromo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone;

6,8-diiodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone; and

6-iodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone; with

6-iodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone being particularly preferred.

Preferred component (2) compounds for these compositions include 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-

(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3*H*-1,2,4-triazol-3-one, fenpropimorph, flusilazole, epoxiconazole and propiconazole. Example compositions of this type include compositions comprising

6-iodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone and 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3*H*-

1,2,4-triazol-3-one in a mole ratio of the compound of Formula Ia to the compound of Formula IIa of from about 4:1 to 1:4, compositions comprising

6-iodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone and fenpropimorph in a mole ratio of the compound of Formula Ia to fenpropimorph of from about 1:1 to 1:10, compositions comprising 6-iodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone and flusilazole in a mole

ratio of the compound of Formula Ia to flusilazole of from about 4:1 to 1:4, and

compositions comprising 6-iodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone; 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-

(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3*H*-1,2,4-triazol-3-one; and flusilazole in a mole ratio of the compound of Formula Ia to the total of the

compound of Formula IIa plus flusilazole of from about 4:1 to 1:4 and a mole ratio of the compound of Formula IIa to flusilazole of from about 4:1 to 1:4.

This invention also provides a process for controlling wheat powdery mildew which comprises applying to the plant or portion thereof to be protected, or to the plant seed or seedling to be protected, an effective amount of a fungicidal combination including component (1) and component (2) wherein the mole ratio of component (1) to component (2) is from about 4:1 to 1:10 (preferably from about 4:1 to 1:4).

Component (1) can, for example, be applied at a rate of 0.2 g/ha or more. Typically component (1) is applied at a rate of 100 g/ha. Component (2) may be applied

simultaneously (e.g., in the form of a composition comprising component (1) and component (2) in an appropriate mole ratio); or component (1) and component (2) can be applied separately in an appropriate mole ratio (e.g., as a tank mix).

Compositions wherein component (2) is selected from the group consisting of 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3*H*-1,2,4-triazol-3-one, kresoxim-methyl, azoxystrobin, (*E*)-2-(methoxyimino)-*N*-methyl-2-(2-phenoxyphenyl)acetamide, flusilazole, epoxiconazole, fenpropimorph, propiconazole and tebuconazole; and wherein the mole ratio of component (1) to component (2) is from about 30:1 to 1:30 are considered especially useful for controlling wheat leaf rust. Preferred component (1) compounds for these compositions include 6-bromo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone; 6,8-diiodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone; and 6-iodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone; with 6-iodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone being particularly preferred being particularly preferred. Preferred component (2) compounds for these compositions include 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3*H*-1,2,4-triazol-3-one, epoxiconazole, flusilazole and tebuconazole; with flusilazole and epoxiconazole being particularly preferred. Preferably, the mole ratio of component (1) to component (2) for these compositions is from about 4:1 to 1:4. Example compositions of this type include compositions comprising 6-iodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone and flusilazole in a mole ratio of the compound of Formula Ia to flusilazole of from about 15:1 to 1:15, compositions comprising 6-iodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone and tebuconazole in a mole ratio of the compound of Formula Ia to tebuconazole from about 30:1 to 1:30.

This invention also provides a process for controlling wheat leaf rust which comprises applying to the plant or portion thereof to be protected, or to the plant seed or seedling to be protected, an effective amount of a fungicidal combination including component (1) and component (2) wherein the mole ratio of component (1) to component (2) is from about 30:1 to 1:30 (preferably from about 4:1 to 1:4). Component (2) can, for example, be applied at a rate of 12.5 g/ha or more. Typically component (2) is applied at a rate of 160 g/ha. Component (1) may be applied simultaneously (e.g., in the form of a composition comprising component (1) and component (2) in an appropriate mole ratio); or component (1) and component (2) can be applied separately in an appropriate mole ratio (e.g., as a tank mix).

Compositions wherein component (2) is selected from the group consisting of 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-

(trifluoromethyl)phenyl]ethylidene]amino]oxy)methyl]phenyl]-3*H*-1,2,4-triazol-3-one, kresoxim-methyl, azoxystrobin, (*E*)-2-(methoxyimino)-*N*-methyl-2-(2-phenoxyphenyl)acetamide, flusilazole, epoxiconazole, fenpropimorph, propiconazole and tebuconazole; and wherein the mole ratio of component (1) to component (2) is from about 15:1 to 1:15 are considered especially useful for controlling wheat foot rot. Preferred component (1) compounds for these compositions include 6-bromo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone; 6,8-diiodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone; and 6-iodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone; with 6-iodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone being particularly preferred being particularly preferred. A particularly preferred component (2) compound for these compositions is flusilazole. Preferably, the mole ratio of component (1) to component (2) for these compositions is from about 4:1 to 1:4. Example compositions of this type include compositions comprising 6-iodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone and flusilazole in a mole ratio of the compound of Formula Ia to flusilazole of from about 15:1 to 1:15.

This invention also provides a process for controlling wheat foot rot which comprises applying to the plant or portion thereof to be protected, or to the plant seed or seedling to be protected, an effective amount of a fungicidal combination including component (1) and component (2) wherein the mole ratio of component (1) to component (2) is from about 15:1 to 1:15 (preferably from about 4:1 to 1:4). Component (1) can, for example, be applied at a rate of 5 g/ha or more. Typically component (1) is applied at a rate of 100 g/ha. Component (2) may be applied simultaneously (e.g., in the form of a composition comprising component (1) and component (2) in an appropriate mole ratio); or component (1) and component (2) can be applied separately in an appropriate mole ratio (e.g., as a tank mix).

Compositions wherein component (2) is selected from the group consisting of 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-(trifluoromethyl)phenyl]ethylidene]amino]oxy)methyl]phenyl]-3*H*-1,2,4-triazol-3-one, kresoxim-methyl, azoxystrobin, (*E*)-2-(methoxyimino)-*N*-methyl-2-(2-phenoxyphenyl)acetamide, flusilazole, epoxiconazole, fenpropimorph, propiconazole and tebuconazole; and wherein the mole ratio of component (1) to component (2) is from about 30:1 to 1:30 are considered especially useful for controlling wheat glume blotch. Preferred component (1) compounds for these compositions include 6-bromo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone; 6,8-diiodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone; and 6-iodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone; with 6-iodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone being particularly preferred being

particularly preferred. Preferred component (2) compounds for these compositions include flusilazole and tebuconazole; with flusilazole being particularly preferred. Preferably, the mole ratio of component (1) to component (2) for these compositions is from about 4:1 to 1:4. Example compositions of this type include compositions comprising 6-iodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone and tebuconazole in a mole ratio of the compound of Formula Ia to tebuconazole from about 30:1 to 1:30

This invention also provides a process for controlling wheat glume blotch which comprises applying to the plant or portion thereof to be protected, or to the plant seed or seedling to be protected, an effective amount of a fungicidal combination including component (1) and component (2) wherein the mole ratio of component (1) to component (2) is from about 30:1 to 1:30 (preferably from about 4:1 to 1:4). Component (2) can, for example, be applied at 12.5 g/ha or more. Typically component (2) is applied at a rate of 160 g/ha. Component (1) may be applied simultaneously (e.g., in the form of a composition comprising component (1) and component (2) in an appropriate mole ratio); or component (1) and component (2) can be applied separately in an appropriate mole ratio, e.g., as a tank mix.

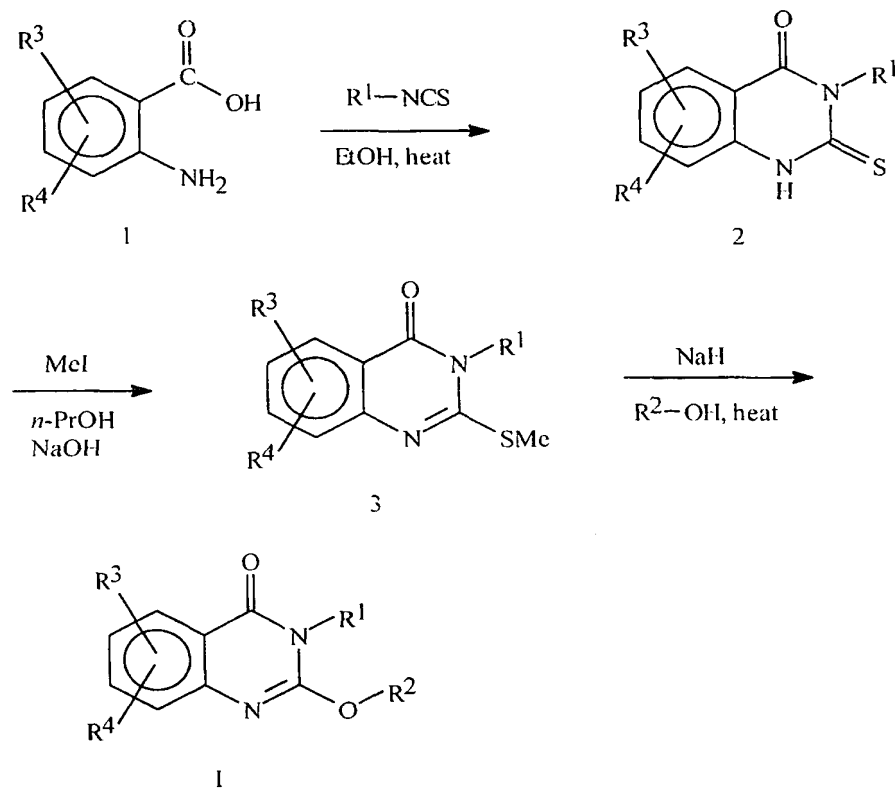
Synthesis of Compounds of Formula I

The compounds of Formula I where D is O can be prepared as described in International Patent Application WO 94/26722 and as shown in Scheme 1.

An anthranilic acid (2-aminobenzoic acid) of Formula 1 is condensed with an isothiocyanate of Formula $R^1\text{-NCS}$ to form the 2-thioquinazolinone of Formula 2. This condensation is preferably performed in the presence of a base such as triethylamine. *S*-Methylation of this compound affords the 2-methylthio-4(3*H*)-quinazolinone of Formula 3.

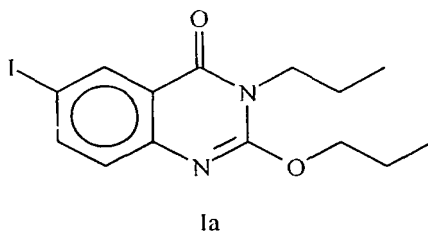
For the introduction of the $R^2\text{O}$ group, the 2-methylthio-4(3*H*)-quinazolinone of Formula 3 is treated with a mixture of a base, for example sodium hydride, in $R^2\text{OH}$ solvent. The reaction mixture is stirred at a temperature from about 0 °C to 120 °C for 1-120 hours. The desired 2- $R^2\text{O}$ -4(3*H*)-quinazolinone can be isolated from the reaction mixture by extraction into a water-immiscible solvent, and purified by chromatography or recrystallization. Similar synthetic procedures are described in U.S. 3,755,582, incorporated herein by reference.

Scheme 1



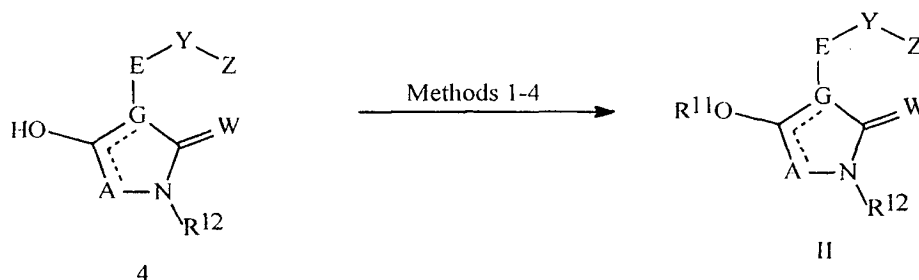
Anthranilic acids of Formula 1 are known or can be prepared by known methods. For example see, March, J. *Advanced Organic Chemistry*; 3rd ed., John Wiley: New York, (1985), p 983. The isothiocyanates of Formula $\text{R}^1\text{-NCS}$ can be prepared from the corresponding amine by treatment with thiophosgene as known in the art. For example, see *J. Heterocycl. Chem.*, (1990), 27, 407.

6-Iodo-3-propyl-2-propyloxy-4(3H)-quinazolinone, Formula Ia, is a compound of Formula I where D is O, R^1 is propyl, R^2 is propyl, R^3 is iodine fixed in the 6 position and R^4 is hydrogen.



Synthesis of Compounds of Formula II

Compounds of Formula II where Q is Q-1 and X is OR¹¹ can be prepared as described in International Patent Application WO 95/14009 by treating a compound of Formula 4 with an appropriate alkyl transfer reagent in an inert solvent with or without additional acidic or basic reagents or other reagents (Scheme 2). Suitable solvents are selected from the group consisting of polar aprotic solvents such as acetonitrile, dimethylformamide or dimethylsulfoxide; ethers such as tetrahydrofuran, dimethoxyethane, or diethyl ether; ketones such as acetone or 2-butanone; hydrocarbons such as toluene or benzene; and halocarbons such as dichloromethane or chloroform.

Scheme 2

Method 1: V-CH=N₂ (V = H or (CH₃)₃Si)

5

Method 2: OR¹¹; Lewis acid

6

Method 3: (R¹¹)₃O⁺ BF₄⁻

7

Method 4: (R¹¹)₂SO₄; R¹¹OSO₂V; or R¹¹-hal;
optional base

(hal = F, Cl, Br, or I)

(V = C₁-C₆ alkyl, C₁-C₆ haloalkyl)

For example, compounds of Formula II where Q is Q-1 and X is OR¹¹ can be prepared by the action of diazoalkane reagents of Formula 5 such as diazomethane (V = H) or trimethylsilyldiazomethane (V = (CH₃)₃Si) on of Formula 4 (Method 1).

Use of trimethylsilyldiazomethane requires a protic cosolvent such as methanol. For examples of these procedures, see *Chem. Pharm. Bull.*, (1984), 32, 3759.

As indicated in Method 2, compounds of Formula II where Q is Q-1 and X is OR¹¹ can also be prepared by contacting compounds of Formula 4 with alkyl

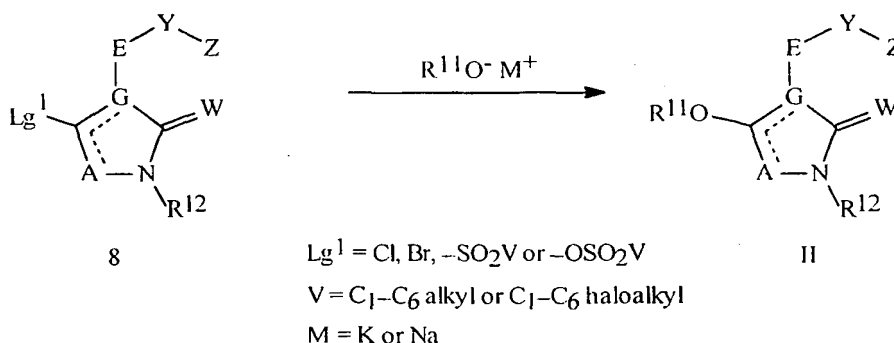
trichloroacetimidates of Formula 6 and a Lewis acid catalyst. Suitable Lewis acids include trimethylsilyl triflate and tetrafluoroboric acid. The alkyl trichloroacetimidates can be prepared from the appropriate alcohol and trichloroacetonitrile as described in the literature (J. Danklmaier and H. Hönig, *Synth. Commun.*, (1990), 20, 203).

5 Compounds of Formula II where Q is Q-1 and X is OR¹¹ can also be prepared from compounds of Formula 4 by treatment with a trialkyloxonium tetrafluoroborate (i.e., Meerwein's salt) of Formula 7 (Method 3). The use of trialkyloxonium salts as powerful alkylating agents is well known in the art (see U. Schöllkopf, U. Groth, C. Deng, *Angew. Chem., Int. Ed. Engl.*, (1981), 20, 798).

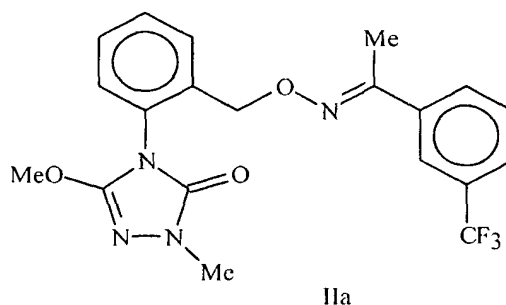
10 Other alkylating agents which can convert compounds of Formula 4 to compounds of Formula II where Q is Q-1 and X is OR¹¹ are dialkyl sulfates such as dimethyl sulfate, haloalkyl sulfonates such as methyl trifluoromethanesulfonate, and alkyl halides such as iodomethane and propargyl bromide (Method 4). These alkylations can be conducted with or without additional base. Appropriate bases include
15 alkali metal alkoxides such as potassium *tert*-butoxide, inorganic bases such as sodium hydride and potassium carbonate, or tertiary amines such as triethylamine, pyridine, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and triethylenediamine. See R. E. Benson, T. L. Cairns, *J. Am. Chem. Soc.*, (1948), 70, 2115 for alkylation examples using agents of this type.

20 Compounds of Formula II where Q is Q-1 and X is OR¹¹ can also be prepared by reaction of Formula 8 compounds with alkali metal alkoxides (R¹¹O⁻M⁺) (Scheme 3). The leaving group Lg¹ in the amides of Formula 8 are any group known in the art to undergo a displacement reaction of this type. Examples of suitable leaving groups include chlorine, bromine, and sulfonyl and sulfonate groups. Examples of suitable
25 inert solvents are dimethylformamide or dimethylsulfoxide.

Scheme 3



2,4-Dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3*H*-1,2,4-triazol-3-one, Formula IIa, is a compound of Formula II where Q is Q-1, E is 1,2-phenylene, A is N, G is N with the floating double bond attached to A, W is O, X is OR¹¹, R¹¹ is CH₃,
 5 R¹² is CH₃, Y is -CHR²⁵O-N=C(R¹⁷)-, R¹⁷ is CH₃, R²⁵ is H, Z is phenyl substituted with R¹⁹ and R¹⁹ is CF₃ fixed in the 3 position.



Azoxystrobin, Formula IIb, is a compound of Formula II where Q is Q-2, E is 1,2 phenylene, W¹ is O, X¹ is C, Y is -O-, Z is 4,6-pyrimidinyl substituted with
 10 R¹⁹, R¹⁹ is phenoxy substituted with R²¹ and R²¹ is cyano fixed in the 2 position.

Kresoxim-methyl, Formula IIc, is a compound of Formula II where Q is Q-2, E is 1,2-phenylene, W¹ is O, X¹ is N, Y is -CHR²⁵O-, R²⁵ is H, Z is phenyl substituted with R¹⁹ and R¹⁹ is CH₃ fixed in the 2 position.

(*E*)-2-(methoxyimino)-*N*-methyl-2-(2-phenoxyphenyl)acetamide, Formula IId, is a
 15 compound of Formula II where Q is Q-2, E is 1,2-phenylene, W¹ is NH, X¹ is N, Y is -O-, Z is phenyl substituted with R¹⁹ wherein R¹⁹ is H.

Without further elaboration, it is believed that one skilled in the art using the preceding description can utilize the present invention to its fullest extent. The following Examples are, therefore, to be construed as merely illustrative.

20 Formulation/Utility

The fungicidal compositions of the present invention comprise an effective amount of a mixture of the compounds(s) of component (1) (e.g., 6-iodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone) and the compound(s) of component (2) (e.g., 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3*H*-1,2,4-triazol-3-one,
 25 kresoxim-methyl, azoxystrobin, (*E*)-2-(methoxyimino)-*N*-methyl-2-(2-phenoxyphenyl)acetamide, flusilazole, epoxiconazole, fenpropimorph, propiconazole and/or tebuconazole). The mixtures of this invention will typically be used as a formulation or composition with an agriculturally suitable carrier comprising at least
 30 one of a liquid diluent, a solid diluent or a surfactant. The formulation or composition

ingredients are selected to be consistent with the physical properties of the active ingredient, mode of application and environmental factors such as soil type, moisture and temperature. Useful formulations include liquids such as solutions (including emulsifiable concentrates), suspensions, emulsions (including microemulsions and/or suspoemulsions) and the like which optionally can be thickened into gels. Useful formulations further include solids such as dusts, powders, granules, pellets, tablets, films, and the like which can be water-dispersible ("wettable") or water-soluble. Active ingredient can be (micro)encapsulated and further formed into a suspension or solid formulation; alternatively the entire formulation of active ingredient can be encapsulated (or "overcoated"). Encapsulation can control or delay release of the active ingredient. Sprayable formulations can be extended in suitable media and used at spray volumes from about one to several hundred liters per hectare. High-strength compositions are primarily used as intermediates for further formulation.

The formulations will typically contain effective amounts of active ingredients, diluent and surfactant within the following approximate ranges which add up to 100 percent by weight.

	Weight Percent		
	<u>Active Ingredients</u>	<u>Diluent</u>	<u>Surfactant</u>
Water-Dispersible and Water-soluble Granules, Tablets and Powders.	5-90	0-94	1-15
Suspensions, Emulsions, Solutions (including Emulsifiable Concentrates)	5-50	40-95	0-15
Dusts	1-25	70-99	0-5
Granules and Pellets	0.01-99	5-99.99	0-15
High Strength Compositions	90-99	0-10	0-2

Typical solid diluents are described in Watkins, et al., *Handbook of Insecticide Dust Diluents and Carriers*, 2nd Ed., Dorland Books, Caldwell, New Jersey. Typical liquid diluents are described in Marsden, *Solvents Guide*, 2nd Ed., Interscience, New York, 1950. *McCutcheon's Detergents and Emulsifiers Annual*, Allured Publ. Corp., Ridgewood, New Jersey, as well as Sisely and Wood, *Encyclopedia of Surface Active Agents*, Chemical Publ. Co., Inc., New York, 1964, list surfactants and recommended uses. All formulations can contain minor amounts of additives to reduce foam, caking, corrosion, microbiological growth and the like, or thickeners to increase viscosity.

Surfactants include, for example, polyethoxylated alcohols, polyethoxylated alkylphenols, polyethoxylated sorbitan fatty acid esters, dialkyl sulfosuccinates, alkyl sulfates, alkylbenzene sulfonates, organosilicones, *N,N*-dialkyltaurates, lignin

sulfonates, naphthalene sulfonate formaldehyde condensates, polycarboxylates, and polyoxyethylene/polyoxypropylene block copolymers. Solid diluents include, for example, clays such as bentonite, montmorillonite, attapulgite and kaolin, starch, sugar, silica, talc, diatomaceous earth, urea, calcium carbonate, sodium carbonate and bicarbonate, and sodium sulfate. Liquid diluents include, for example, water, *N,N*-dimethylformamide, dimethyl sulfoxide, *N*-alkylpyrrolidone, ethylene glycol, polypropylene glycol, paraffins, alkylbenzenes, alkyl naphthalenes, oils of olive, castor, linseed, tung, sesame, corn, peanut, cotton-seed, soybean, rape-seed and coconut, fatty acid esters, ketones such as cyclohexanone, 2-heptanone, isophorone and 4-hydroxy-4-methyl-2-pentanone, and alcohols such as methanol, cyclohexanol, decanol and tetrahydrofurfuryl alcohol.

Solutions, including emulsifiable concentrates, can be prepared by simply mixing the ingredients. Dusts and powders can be prepared by blending and, usually, grinding as in a hammer mill or fluid-energy mill. Suspensions are usually prepared by wet-milling; see, for example, U.S. 3,060,084. Granules and pellets can be prepared by spraying the active material upon preformed granular carriers or by agglomeration techniques. See Browning, "Agglomeration", *Chemical Engineering*, December 4, 1967, pp 147-48, *Perry's Chemical Engineer's Handbook*, 4th Ed., McGraw-Hill, New York, 1963, pages 8-57 and following, and International Patent Publication WO 91/13546. Pellets can be prepared as described in U.S. Patent No. 4,172,714. Water-dispersible and water-soluble granules can be prepared as taught in U.S. Patent No. 4,144,050, U.S. Patent No. 3,920,442 and German Patent Application DE 3,246,493. Tablets can be prepared as taught in U.S. Patent No. 5,180,587, U.S. Patent No. 5,232,701 and U.S. Patent No. 5,208,030. Films can be prepared as taught in Great Britain Patent Application GB 2,095,558 and U.S. Patent No. 3,299,566.

For further information regarding the art of formulation, see U.S. Patent No. 3,235,361, Col. 6, line 16 through Col. 7, line 19 and Examples 10-41; U.S. Patent No. 3,309,192, Col. 5, line 43 through Col. 7, line 62 and Examples 8, 12, 15, 39, 41, 52, 53, 58, 132, 138-140, 162-164, 166, 167 and 169-182; U.S. Patent No. 2,891,855, Col. 3, line 66 through Col. 5, line 17 and Examples 1-4; Klingman, *Weed Control as a Science*, John Wiley and Sons, Inc., New York, 1961, pp 81-96; and Hance et al., *Weed Control Handbook*, 8th Ed., Blackwell Scientific Publications, Oxford, 1989.

In the following Examples, all percentages are by weight and all formulations are prepared in conventional ways.

Example AWettable Powder

	Active ingredient(s)	65.0%
	dodecylphenol polyethylene glycol ether	2.0%
5	sodium ligninsulfonate	4.0%
	sodium silicoaluminate	6.0%
	montmorillonite (calcined)	23.0%.

Example BGranule

10	Active ingredient(s)	10.0%
	attapulgit granules (low volatile matter, 0.71/0.30 mm; U.S.S. No. 25–50 sieves)	90.0%.

Example CExtruded Pellet

15	Active ingredient(s)	25.0%
	anhydrous sodium sulfate	10.0%
	crude calcium ligninsulfonate	5.0%
	sodium alkyl naphthalenesulfonate	1.0%
	calcium/magnesium bentonite	59.0%.

20 Example DEmulsifiable Concentrate

	Active ingredient(s)	20.0%
	blend of oil soluble sulfonates and polyoxyethylene ethers	10.0%
25	isophorone	70.0%.

The compounds of this invention are useful as plant disease control agents. The present invention therefore further comprises a method for controlling plant diseases caused by fungal plant pathogens comprising applying to the plant or portion thereof to be protected, or to the plant seed or seedling to be protected, an effective amount of a compound of the invention or a fungicidal composition containing said compound. The compounds and compositions of this invention provide control of diseases caused by a broad spectrum of fungal plant pathogens in the Basidiomycete, Ascomycete, Oomycete and Deuteromycete classes. They are effective in controlling a broad spectrum of plant diseases, particularly foliar pathogens of ornamental, vegetable, field, cereal, and fruit crops. These pathogens include *Plasmopara viticola*, *Phytophthora infestans*, *Peronospora tabacina*, *Pseudoperonospora cubensis*, *Pythium aphanidermatum*, *Alternaria brassicae*, *Septoria nodorum*, *Septoria tritici*, *Cercosporidium personatum*, *Cercospora arachidicola*, *Pseudocercospora herpotrichoides*, *Cercospora beticola*,

- Botrytis cinerea*, *Monilinia fructicola*, *Pyricularia oryzae*, *Podosphaera leucotricha*, *Venturia inaequalis*, *Erysiphe graminis*, *Uncinula necatur*, *Puccinia recondita*, *Puccinia graminis*, *Hemileia vastatrix*, *Puccinia striiformis*, *Puccinia arachidis*, *Rhizoctonia solani*, *Sphaerotheca fuliginea*, *Fusarium oxysporum*, *Verticillium dahliae*,
 5 *Pythium aphanidermatum*, *Phytophthora megasperma*, *Sclerotinia sclerotiorum*, *Sclerotium rolfsii*, *Erysiphe polygoni*, *Pyrenophora teres*, *Gaeumannomyces graminis*, *Rhynchosporium secalis*, *Fusarium roseum*, *Bremia lactucae* and other genera and species closely related to these pathogens.

- Mixtures of this invention can be further mixed with one or more other
 10 insecticides, fungicides, nematocides, bactericides, acaricides, growth regulators, chemosterilants, semiochemicals, repellents, attractants, pheromones, feeding stimulants or other biologically active compounds to form a multi-component pesticide giving an even broader spectrum of agricultural protection. Examples of such agricultural
 15 protectants with which compounds of this invention can be formulated are: insecticides such as abamectin, acephate, azinphos-methyl, bifenthrin, buprofezin, carbofuran, chlorfenapyr, chlorpyrifos, chlorpyrifos-methyl, cyfluthrin, beta-cyfluthrin, cyhalothrin, lambda-cyhalothrin, deltamethrin, diafenthiuron, diazinon, diflubenzuron, dimethoate, esfenvalerate, fenoxycarb, fenpropathrin, fenvalerate, fipronil, flucythrinate, tau-fluvalinate, fonophos, imidacloprid, isofenphos, malathion, metaldehyde,
 20 methamidophos, methidathion, methomyl, methoprene, methoxychlor, methyl 7-chloro-2,5-dihydro-2-[[N-(methoxycarbonyl)-N-[4-(trifluoromethoxy)phenyl]amino]carbonyl]indeno[1,2-e][1,3,4]oxadiazine-4a(3H)-carboxylate (DPX-JW062), monocrotophos, oxamyl, parathion, parathion-methyl, permethrin, phorate, phosalone, phosmet, phosphamidon, pirimicarb, profenofos,
 25 rotenone, sulprofos, tebufenozide, tefluthrin, terbufos, tetrachlorvinphos, thiodicarb, tralomethrin, trichlorfon and triflumuron; fungicides such as benomyl, blasticidin-S, Bordeaux mixture (tribasic copper sulfate), captan, carbendazim, chloroneb, chlorothalonil, copper oxychloride, copper salts, cymoxanil, cyprodinil (CGA 219417), diclomezine, dicloran, dimethomorph, dodine, edifenphos, famoxadone, fenpiclonil, fluazinam, flutolanil, folpet, fosetyl-aluminum, furalaxyl, iprobenfos, iprodione,
 30 isoprothiolane, kasugamycin, mancozeb, maneb, mepronil, metalaxyl, S-methyl 7-benzothiazolecarbothioate (CGA 245704), myclobutanil, neo-asozin (ferric methancarsonate), oxadixyl, pencycuron, probenazole, prochloraz, pyrifenoxy, pyroquilon, quinoxifen, spiroxamine (KWG4168), sulfur, thiabendazole,
 35 thiophanate-methyl, thiram, tricyclazole, validamycin and vinclozolin; nematocides such as aldoxycarb and fenamiphos; bactericides such as streptomycin; acaricides such as amitraz, chinomethionat, chlorobenzilate, cyhexatin, dicofol, dienochlor, etoxazole, fenazaquin, fenbutatin oxide, fenpropathrin, fenpyroximate, hexythiazox, propargite,

pyridaben and tebufenpyrad; and biological agents such as *Bacillus thuringiensis*, *Bacillus thuringiensis* delta endotoxin, baculovirus, and entomopathogenic bacteria, virus and fungi.

5 In certain instances, combinations with other fungicides having a similar spectrum of control but a different mode of action will be particularly advantageous for resistance management.

10 Plant disease control is ordinarily accomplished by applying an effective amount of the composition of this invention either pre— or post—infection, to the portion of the plant to be protected such as the roots, stems, foliage, fruit, seeds, tubers or bulbs, or to the media (soil or sand) in which the plants to be protected are growing. The composition can also be applied to the seed to protect the seed and seedling.

15 Rates of application for this composition can be influenced by many factors of the environment and should be determined under actual use conditions. Foliage can normally be protected when treated at a rate of from less than 1 g/ha to 5,000 g/ha of aggregate active ingredient. Aggregate active ingredient is defined as the total combined weight of active ingredients. Seed and seedlings can normally be protected when seed is treated at a rate of from 0.1 to 10 g of aggregate active ingredient per kilogram of seed.

20 The following Examples demonstrate the composition and method of the present invention and provide experimental evidence for synergy between the compound of Formula Ia and flusilazole in preventative control of wheat leaf rust caused by *Puccinia recondita*, wheat foot rot caused by *Pseudocercospora herpotrichoides*, and wheat glume blotch caused by *Septoria nodorum*. The experimental also provides evidence for synergy between the compound of Formula Ia and tebuconazole in preventative control of wheat leaf rust and wheat glume blotch. The experimental also provides evidence for synergy between the compound of Formula Ia and flusilazole in curative control of wheat powdery mildew caused by *Erysiphe graminis f. sp. tritici* and wheat leaf rust.

30 The experimental also provides evidence for synergy between the compounds of Formula Ia, Formula IIa and flusilazole in preventative control of wheat foot rot. The experimental also provides evidence for synergy between the compounds of Formula Ia, IIa and flusilazole in curative control of wheat powdery mildew. The pathogen control protection afforded by these compositions is not limited, however, to these species.

35 The following TESTS demonstrate the control efficacy of compounds of this invention on specific pathogens. The pathogen control protection afforded by the compounds is not limited, however, to these species.

BIOLOGICAL EXAMPLES OF THE INVENTION

Test compounds were first dissolved in acetone in an amount equal to 50% of the final volume and then suspended at a concentrations from 0.08 to 200 ppm in purified water containing 250 ppm of the surfactant Trem[®] 014 (polyhydric alcohol esters).

- 5 The resulting test suspensions were then used in the following test protocols. Spraying these test suspensions to the point of run-off on the test plants is the equivalent of a rate of 500 g/ha.

Protocol # 1 - WPM Preventive

- 10 The test compounds were sprayed to the point of run-off on wheat seedlings. The following day the seedlings were inoculated with a spore dust of *Erysiphe graminis* f. sp. *tritici*, (the causal agent of wheat powdery mildew). Seedlings were incubated in a growth chamber at 20 °C for 6 days, after which disease ratings were made.

Protocol # 2 - WPM Curative

- 15 Wheat seedlings were inoculated with a spore dust of *Erysiphe graminis* f. sp. *tritici*, (the causal agent of wheat powdery mildew). The following day a test compounds were sprayed to the point of run-off on and seedlings incubated in a growthchamber at 20 °C for 7 days, after which disease ratings were made.

Protocol # 3 WLR Preventive

- 20 The test compounds were sprayed to the point of run-off on wheat seedlings. The following day the seedlings were inoculated with a spore suspension of *Puccinia recondita* (the causal agent of wheat leaf rust) and incubated in a saturated atmosphere at 20 °C for 24 h, and then moved to a growth chamber at 20 °C for 6 days, after which disease ratings were made.

Protocol # 4 - WLR Curative

- 25 Wheat seedlings were inoculated with a spore suspension of *Puccinia recondita* (the causal agent of wheat leaf rust). The following day the test compounds were sprayed to the point of run-off on and incubated in a saturated atmosphere at 20 °C for 24 h, then moved to a growth chamber at 20 °C for 6 days, after which disease ratings were made.

- 30 Protocol # 5 - WFR Preventive

The test compounds were sprayed to the point of run-off on wheat seedlings. The following day the seedlings were inoculated with a spore suspension of *Pseudocercospora herpotrichoides* (the causal agent of wheat eye spot or wheat foot rot) and incubated in a saturated atmosphere at 20 °C for 72 h, and then moved to a growth chamber at 20 °C for 6 days, after which disease ratings were made.

Protocol # 6 - WGB Preventive

The test compounds were sprayed to the point of run-off on wheat seedlings. The following day the seedlings were inoculated with a spore suspension of *Septoria*

nodorum (the causal agent of wheat glume blotch) and incubated in a saturated atmosphere at 20 °C for 48 h, and then moved to a growth chamber at 20 °C for 6 days, after which disease ratings were made.

Protocol # 7 - WGB Curative

- 5 Wheat seedlings were inoculated with a spore suspension *Septoria nodorum* (the causal agent of wheat glume blotch). Two days later test compounds were sprayed to the point of run-off on and seedlings incubated in a saturated atmosphere at 20 °C for 48 h, then moved to a growth chamber at 20 °C for 6 days, after which disease ratings were made.

Protocol # 8 - WPM Preventative

- 10 The test suspension was sprayed to the point of run-off on wheat seedlings. The following day the seedlings were inoculated with a spore dust of *Erysiphe graminis f. sp. tritici*, (the causal agent of wheat powdery mildew) and incubated in a growth chamber at 20 °C for 7 days, after which disease ratings were made.

- 15 Results for protocols 1 - 8 are given in Tables A-G. In the tables, a rating of 100 indicates 100% disease control and a rating of 0 indicates no disease control (relative to the controls). An (nt) indicates no test results and (--) indicates no estimate of activity. In Tables A-G rates are given in parts per million (ppm) and/or grams active ingredient per hectare (g a.i./ha). The term "Actual" stands for the experimental value. The
20 abbreviation "Exp." stands for "Expected" (i.e., the predicted activity, p, from the Colby equation).

TABLE A
Synergistic Effects of Compound Ia in Combination with Flusilazole, Tebuconazole and Prochloraz for Preventive Control of
Wheat Powdery Mildew (WPM), Wheat Leaf Rust (WLR), Wheat Foot Rot (WFR) and Wheat Glume Blotch (WGB)

<u>Test</u> <u>Cmpd 1</u>	<u>Test</u> <u>Cmpd 2</u>	<u>Rates</u> <u>(ppm)</u>	<u>Rates</u> <u>(g a.i./ha)</u>	<u>Mole</u> <u>Ratio</u>	<u>Percent Disease Control</u>							
					<u>WPM⁽¹⁾</u>		<u>WLR⁽²⁾</u>		<u>WFR⁽³⁾</u>		<u>WGB⁽⁴⁾</u>	
					<u>Actual⁽⁵⁾</u>	<u>Exp.⁽⁶⁾</u>	<u>Actual</u>	<u>Exp.</u>	<u>Actual</u>	<u>Exp.</u>	<u>Actual</u>	<u>Exp.</u>
Ia	--	0.08	0.2		100	-- ⁽⁷⁾	0	--	0	--	0	--
Ia	--	0.4	1		100	--	9	--	0	--	0	--
Ia	--	2	5		100	--	0	--	0	--	0	--
Ia	--	10	25		100	--	0	--	0	--	0	--
Flusilazole	--	0.08	0.2		90	--	18	--	16	--	0	--
Flusilazole	--	0.4	1		99	--	9	--	54	--	0	--
Flusilazole	--	2	5		100	--	88	--	45	--	0	--
Flusilazole	--	1	2.5		62	--	27	--	50	--	60	--
Flusilazole	--	5	12.5		35	--	79	--	100	--	83	--
Flusilazole	--	20	50		81	--	100	--	100	--	100	--
Flusilazole	Ia	0.08 + 0.08	0.2 + 0.2	1.18:1	100	100	9	18	0	16	0	0
Flusilazole	Ia	0.4 + 0.4	1 + 1	1.18:1	100	100	18	17	8	54	0	0
Flusilazole	Ia	2 + 2	5 + 5	1.18:1	100	100	88	88	100	45	0	0
Flusilazole	Ia	1 + 2	2.5 + 5	1:1.69	100	100	32	27	81	50	43	60
Flusilazole	Ia	5 + 2	12.5 + 5	2.95:1	nt ⁽⁸⁾	--	98	79	100	100	91	83
Flusilazole	Ia	20 + 2	50 + 5	11.81:1	nt	--	99	100	100	100	99	100

Percent Disease Control														
Test	Cmpd 1	Test	Cmpd 2	Rates (ppm)	Rates (g a.i./ha)	Mole Ratio	WPM ⁽¹⁾		WLR ⁽²⁾		WFR ⁽³⁾		WGB ⁽⁴⁾	
							Actual ⁽⁵⁾	Exp. ⁽⁶⁾	Actual	Exp.	Actual	Exp.	Actual	Exp.
Flusilazole		la		1 + 10	2.5 + 25	1:8.47	nt	--	70	27	96	50	38	60
Flusilazole		la		5 + 10	12.5 + 25	1:1.69	nt	--	100	79	100	100	94	83
Flusilazole		la		20 + 10	50 + 25	2.36:1	nt	--	100	100	100	100	100	100
Tebuconazole		--		0.4	1		nt	--	32	--	nt	--	nt	--
Tebuconazole		--		2	5		nt	--	100	--	nt	--	55	--
Tebuconazole		--		10	25		nt	--	100	--	nt	--	96	--
Tebuconazole		--		40	100		nt	--	nt	--	nt	--	100	--
Tebuconazole		la		0.4 + 2	1 + 5	1:4.13	nt	--	98	32	nt	--	--	--
Tebuconazole		la		2 + 2	5 + 5	1:1.21	nt	--	100	100	nt	--	59	55
Tebuconazole		la		10 + 2	25 + 5	6.06:1	nt	--	100	100	nt	--	100	96
Tebuconazole		la		40 + 2	100 + 5	24.23:1	nt	--		--	nt	--	100	100
Tebuconazole		la		0.4 + 10	1 + 25	1:20.63	nt	--	76	32	nt	--	nt	--
Tebuconazole		la		2 + 10	5 + 25	1:4.13	nt	--	99	100	nt	--	84	55
Tebuconazole		la		10 + 10	25 + 25	1:1.21	nt	--	100	100	nt	--	100	96
Tebuconazole		la		40 + 10	100 + 25	4.85:1	nt	--	nt	--	nt	--	100	100
Prochloraz		--		0.4	1		nt	--	nt	--	37	--	nt	--
Prochloraz		--		2	5		nt	--	nt	--	100	--	nt	--
Prochloraz		--		10	25		nt	--	nt	--	100	--	nt	--
Prochloraz		la		0.4 + 2	1 + 5	1:5	nt	--	nt	--	37	37	nt	--
Prochloraz		la		2 + 2	5 + 5	1:1	nt	--	nt	--	100	100	nt	--

<u>Test</u>	<u>Cmpd 1</u>	<u>Test</u> <u>Cmpd 2</u>	<u>Rates</u> <u>(ppm)</u>	<u>Rates</u> <u>(g a.i./ha)</u>	<u>Mole</u> <u>Ratio</u>	<u>Percent Disease Control</u>							
						<u>WPM⁽¹⁾</u>		<u>WLR⁽²⁾</u>		<u>WFR⁽³⁾</u>		<u>WGB⁽⁴⁾</u>	
						<u>Actual⁽⁵⁾</u>	<u>Exp.⁽⁶⁾</u>	<u>Actual</u>	<u>Exp.</u>	<u>Actual</u>	<u>Exp.</u>	<u>Actual</u>	<u>Exp.</u>
Prochloraz		Ia	10 + 2	25 + 5	5:1	nt	--	nt	--	100	100	nt	--
Prochloraz		Ia	0.4 + 10	1 + 25	1:25	nt	--	nt	--	37	37	nt	--
Prochloraz		Ia	2 + 10	5 + 25	1:5	nt	--	nt	--	100	100	nt	--
Prochloraz		Ia	10 + 10	25 + 25	1:1	nt	--	nt	--	100	100	nt	--

(1) Wheat powdery mildew activity - Protocol #1

(2) Wheat leaf rust activity - Protocol # 3

(3) Wheat foot rot activity - Protocol # 5

(4) Wheat glume blotch activity - Protocol # 6

(5) Actual activity observed in the test

(6) Predicted activity

(7) No estimate - (--)

(8) Not tested (nt)

TABLE B
**Synergistic Effects of Compound Ia in Combination with Flusilazole or Tebuconazole for Curative Control of Wheat Powdery Mildew (WPM),
Wheat Leaf Rust (WLR) and Wheat Glume Blotch (WGB)**

<u>Test</u> <u>Cmpd 1</u>	<u>Test</u> <u>Cmpd 2</u>	<u>Rates</u> <u>(ppm)</u>	<u>Rates</u> <u>(g a.i./ha)</u>	<u>Mole</u> <u>Ratio</u>	<u>Percent Disease Control</u>					
					<u>WPM⁽¹⁾</u>		<u>WLR⁽²⁾</u>		<u>WGB⁽³⁾</u>	
					<u>Actual</u>	<u>Exp.</u>	<u>Actual</u>	<u>Exp.</u>	<u>Actual</u>	<u>Exp.</u>
Ia	--	0.08	0.2		0	--	0	--	0	--
Ia	--	0.4	1		56	--	0	--	0	--
Ia	--	2	5		60	--	0	--	10	--
Ia	--	10	25		nt	--	0	--	0	--
Flusilazole	--	0.08	0.2		68	--	0	--	0	--
Flusilazole	--	0.4	1		73	--	0	--	0	--
Flusilazole	--	1	2.5		68	--	43	--	5	--
Flusilazole	--	2	5		100	--	80	--	0	--
Flusilazole	--	5	12.5		91	--	84	--	15	--
Flusilazole	--	20	50		100	--	100	--	69	--
Flusilazole	Ia	0.08 + 0.08	0.2 + 0.2	1.18:1	98	68	nt	--	nt	--
Flusilazole	Ia	0.4 + 0.4	1 + 1	1.18:1	100	82	nt	--	nt	--
Flusilazole	Ia	2 + 2	5 + 5	1.18:1	100	100	nt	--	nt	--
Flusilazole	Ia	1 + 2	2.5 + 5	1:1.69	nt	--	15	43	0	15
Flusilazole	Ia	5 + 2	12.5 + 5	2.95:1	nt	--	100	84	43	23
Flusilazole	Ia	20 + 2	50 + 5	11.81:1	nt	--	99	100	71	72

Test Cmpd 1	Test Cmpd 2	Rates (ppm)	Rates (g a.i./ha)	Mole Ratio	Percent Disease Control			
					WPM ⁽¹⁾		WLR ⁽²⁾	
					Actual	Exp.	Actual	Exp.
Flusilazole	Ia	1 + 10	2.5 + 25	1:8.47	nt	--	71	43
Flusilazole	Ia	5 + 10	12.5 + 25	1:1.69	nt	--	100	84
Flusilazole	Ia	20 + 10	50 + 25	2.36:1	nt	--	100	100
Tebuconazole	--	0.4	1		nt	--	40	--
Tebuconazole	--	2	5		nt	--	100	--
Tebuconazole	--	10	25		nt	--	100	--
Tebuconazole	--	40	100		nt	--	100	--
Tebuconazole	Ia	0.4 + 2	1 + 5	1:4.13	nt	--	100	40
Tebuconazole	Ia	2 + 2	5 + 5	1:1.21	nt	--	100	100
Tebuconazole	Ia	10 + 2	25 + 5	6.06:1	nt	--	100	100
Tebuconazole	Ia	40 + 2	100 + 5	24.23:1	nt	--	100	100
Tebuconazole	Ia	0.4 + 10	1 + 25	1:20.63	nt	--	100	40
Tebuconazole	Ia	2 + 10	5 + 25	1:4.13	nt	--	100	100
Tebuconazole	Ia	10 + 10	25 + 25	1:1.21	nt	--	100	100
Tebuconazole	Ia	40 + 10	100 + 25	4.85:1	nt	--	100	100

(1) Wheat powdery mildew - Protocol # 2

(2) Wheat leaf rust - Protocol # 4

(3) Wheat glume blotch - Protocol # 7

TABLE C

Synergistic Effects of Compound Ia in Combination with Compound IIa for Preventive Control of Wheat Powdery Mildew (WPM), Wheat Leaf Rust (WLR), Wheat Foot Rot (WFR) and Wheat Glume Blotch (WGB)

Test Cmpd 1	Test Cmpd 2	Test Cmpd 3	Rates (ppm)	Rates (g a.i./ha)	Mole Ratio	WPM ⁽¹⁾		WLR ⁽²⁾		WFR ⁽³⁾		WGB ⁽⁴⁾	
						Actual	Exp.	Actual	Exp.	Actual	Exp.	Actual	Exp.
Ia	--	--	0.08	0.2		100	--	0	--	0	--	0	--
Ia	--	--	0.4	1		100	--	9	--	0	--	0	--
Ia	--	--	2	5		100	--	0	--	0	--	0	--
IIa	--	--	0.08	0.2		60	--	54	--	8	--	0	--
IIa	--	--	0.4	1		88	--	91	--	26	--	0	--
IIa	--	--	2	5		100	--	99	--	38	--	0	--
IIa	Ia	--	0.08 + 0.08	0.2 + 0.2	1:1.13	99	100	54	54	0	8	0	0
IIa	Ia	--	0.4 + 0.4	1 + 1	1:1.13	100	100	93	92	8	26	0	0
IIa	Ia	--	2 + 2	5 + 5	1:1.13	100	100	99	91	61	38	0	0

42

(1) Wheat powdery mildew activity - Protocol #1

(3) Wheat foot rot activity - Protocol # 5

(2) Wheat leaf rust activity - Protocol # 3

(4) Wheat glume blotch activity - Protocol # 6

TABLE D

Synergistic Effects of Compound Ia in Combination with Compound IIa on Curative Control of Wheat Powdery Mildew (WPM), Wheat Leaf Rust (WLR) and Wheat Glume Blotch (WGB)

Test Cmpd 1	Test Cmpd 2	Test Cmpd 3	Rates (ppm)	Rates (g a.i./ha)	Mole Ratio	Percent Disease Control					
						WPM ⁽¹⁾		WLR ⁽²⁾		WGB ⁽³⁾	
						Actual	Exp.	Actual	Exp.	Actual	Exp.
Ia	--	--	0.08	0.2		0	--	0	--	0	--
Ia	--	--	0.4	1		56	--	0	--	0	--
Ia	--	--	2	5		60	--	0	--	10	--
IIa	--	--	0.08	0.2		0	--	0	--	13	--
IIa	--	--	0.4	1		73	--	0	--	0	--
IIa	--	--	2	5		100	--	0	--	13	--
IIa	Ia	--	0.08 + 0.08	0.2 + 0.2	1:1.13	21	0	0	0	0	13
IIa	Ia	--	0.4 + 0.4	1 + 1	1:1.13	99	88	0	0	13	0
IIa	Ia	--	2 + 2	5 + 5	1:1.13	100	100	0	0	53	22

(1) Wheat powdery mildew - Protocol # 2

(2) Wheat leaf rust - Protocol # 4

(3) Wheat glume blotch - Protocol # 7

TABLE E
Synergistic Effects of Compound Ia / Compound IIa / Flusilazole combinations for Preventive Control of Wheat Powdery Mildew (WPM),
Wheat Leaf Rust (WLR), Wheat Foot Rot (WFR) and Wheat Glume Blotch (WGB)

Percent Disease Control																		
Test	Cmpd 1	Test	Cmpd 2	Test	Cmpd 3	Rates (ppm)	Rates (g a.i./ha)	Mole Ratio	WPM ⁽¹⁾				WLR ⁽²⁾		WFR ⁽³⁾		WGB ⁽⁴⁾	
									Actual	Exp.	Actual	Exp.	Actual	Exp.	Actual	Exp.	Actual	Exp.
	Ia	--	--	--	--	0.08	0.2		100	--	0	--	0	--	0	--	0	--
	Ia	--	--	--	--	0.4	1		100	--	9	--	0	--	0	--	0	--
	Ia	--	--	--	--	2	5		100	--	0	--	0	--	0	--	0	--
	IIa	--	--	--	--	0.08	0.2		60	--	54	--	8	--	0	--	0	--
	IIa	--	--	--	--	0.4	1		88	--	91	--	26	--	0	--	0	--
	IIa	--	--	--	--	2	5		100	--	99	--	38	--	0	--	0	--
	Flusilazole	--	--	--	--	0.08	0.2		90	--	18	--	16	--	0	--	0	--
	Flusilazole	--	--	--	--	0.4	1		99	--	9	--	54	--	0	--	0	--
	Flusilazole	--	--	--	--	2	5		100	--	88	--	45	--	0	--	0	--
	Flusilazole	Ia	Ia	IIa	IIa	0.08 + 0.08 + 0.08	0.2 + 0.2 + 0.2	1.33:1.13:1	100	100	28	62	8	16	0	0	0	0
	Flusilazole	Ia	Ia	IIa	IIa	0.4 + 0.4 + 0.4	1 + 1 + 1	1.33:1.13:1	100	100	93	100	62	54	0	0	0	0
	Flusilazole	Ia	Ia	IIa	IIa	2 + 2 + 2	5 + 5 + 5	1.33:1.13:1	100	100	99	100	100	45	47	0	0	0

(1) Wheat powdery mildew activity - Protocol #1

(2) Wheat leaf rust activity - Protocol # 3

(3) Wheat foot rot activity - Protocol # 5

(4) Wheat glume blotch activity - Protocol # 6

TABLE F
Synergistic Effects of Compound Ia / Compound IIa / Flusilazole on Curative Control of Wheat Powdery Mildew (WPM),
Wheat Leaf Rust (WLR) and Wheat Glume Blotch (WGB)

<u>Test</u> <u>Cmpd 1</u>	<u>Test</u> <u>Cmpd 2</u>	<u>Test</u> <u>Cmpd 3</u>	<u>Rates</u> <u>(ppm)</u>	<u>Rates</u> <u>(g a.i./ha)</u>	<u>Mole</u> <u>Ratio</u>	<u>Percent Disease Control</u>					
						<u>WPM⁽¹⁾</u>		<u>WLR⁽²⁾</u>		<u>WGB⁽³⁾</u>	
						<u>Actual</u>	<u>Exp.</u>	<u>Actual</u>	<u>Exp.</u>	<u>Actual</u>	<u>Exp.</u>
Ia	--	--	0.08	0.2		0	--	0	--	0	--
Ia	--	--	0.4	1		56	--	0	--	0	--
Ia	--	--	2	5		60	--	0	--	10	--
IIa	--	--	0.08	0.2		0	--	0	--	13	--
IIa	--	--	0.4	1		73	--	0	--	0	--
IIa	--	--	2	5		100	--	0	--	13	--
Flusilazole	--	--	0.08	0.2		68	--	0	--	0	--
Flusilazole	--	--	0.4	1		73	--	0	--	0	--
Flusilazole	--	--	2	5		100	--	80	--	0	--
Flusilazole	Ia	IIa	0.08 + 0.08 + 0.08	0.2 + 0.2 + 0.2	1.33:1.13:1	96	68	0	0	40	13
Flusilazole	Ia	IIa	0.4 + 0.4 + 0.4	1 + 1 + 1	1.33:1.13:1	100	100	0	0	0	0
Flusilazole	Ia	IIa	2 + 2 + 2	5 + 5 + 5	1.33:1.13:1	100	100	86	80	13	22

(1) Wheat powdery mildew - Protocol # 2

(2) Wheat leaf rust - Protocol # 4

(3) Wheat glume blotch - Protocol # 7

TABLE G

Synergistic Effects of Compound Ia in Combination with Fenpropimorph for Preventative Control of Wheat Powdery Mildew (WPM)(1)

<u>Compd 1</u>	<u>Compd 2</u>	<u>Rates (g a.i./ha)</u>	<u>Mole Ratio</u>	<u>% Control of WPM(2)</u>			
				<u>Test 1</u>	<u>Test 2</u>	<u>Test 3</u>	<u>Mean</u>
Ia	--	20		100	100	100	100
Ia	--	5		96	95	97	96
Ia	--	1		94	87	34	72
Fenpropimorph	--	100		79	76	80	78
Fenpropimorph	--	20		34	76	13	41
Fenpropimorph	--	5		0	nt(5)	0	0
Fenpropimorph	Ia	100 + 20	6.1:1	100	100	100	100
Fenpropimorph	Ia	20 + 5	4.9:1	99	100	98	99
Fenpropimorph	Ia	5 + 1	6.1:1	92	nt	82	87

Untreated

(% area diseased)

Foliage)

(1) Wheat powdery mildew activity - Protocol #8

(2) Actual activity observed in the test

(3) Predicted activity

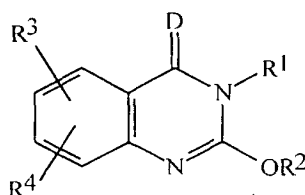
(4) No estimate - (--)

(5) Not tested (nt)

CLAIMS

What is claimed is:

1. A fungicidal composition comprising:
 - (1) at least one compound selected from the quinazolinones of Formula I,
- 5 *N*-oxides, and agriculturally suitable salts thereof,



I

wherein

D is O or S;

- 10 R^1 is C_1 - C_{10} alkyl; C_3 - C_5 cycloalkyl; C_3 - C_{10} alkenyl; C_3 - C_{10} alkynyl; C_1 - C_{10} haloalkyl; C_3 - C_{10} haloalkenyl; C_3 - C_{10} haloalkynyl; C_2 - C_{10} alkoxyalkyl; C_2 - C_{10} alkylthioalkyl; C_2 - C_{10} alkylsulfinylalkyl; C_2 - C_{10} alkylsulfonylalkyl; C_4 - C_{10} cycloalkylalkyl; C_4 - C_{10} alkenyloxyalkyl; C_4 - C_{10} alkynyloxyalkyl; C_4 - C_{10} (cycloalkyl)oxyalkyl; C_4 - C_{10} alkenylthioalkyl; C_4 - C_{10} alkynylthioalkyl; C_4 - C_{10} (cycloalkyl)thioalkyl; C_2 - C_{10} haloalkoxyalkyl; C_4 - C_{10} haloalkenyloxyalkyl; C_4 - C_{10} haloalkynyloxyalkyl; C_4 - C_{10} alkoxyalkenyl; C_4 - C_{10} alkoxyalkynyl; C_4 - C_{10} alkylthioalkenyl; C_4 - C_{10} alkylthioalkynyl; C_4 - C_{10} trialkylsilylalkyl; C_1 - C_{10} alkyl substituted with NR^5R^6 , nitro, cyano or phenyl optionally substituted with R^8 , R^9 and R^{10} ; C_1 - C_{10} alkoxy; C_1 - C_{10} haloalkoxy; C_1 - C_{10} alkylthio; C_1 - C_{10} haloalkylthio; or pyridinyl, furanyl, thienyl, naphthalenyl, benzofuranyl, benzothienyl or quinolinyl each optionally substituted with R^8 , R^9 and R^{10} ;
- 25 R^2 is C_1 - C_{10} alkyl; C_3 - C_7 cycloalkyl; C_3 - C_{10} alkenyl; C_3 - C_{10} alkynyl; C_1 - C_{10} haloalkyl; C_3 - C_{10} haloalkenyl; C_3 - C_{10} haloalkynyl; C_2 - C_{10} alkoxyalkyl; C_2 - C_{10} alkylthioalkyl; C_2 - C_{10} alkylsulfinylalkyl; C_2 - C_{10} alkylsulfonylalkyl; C_4 - C_{10} cycloalkylalkyl; C_4 - C_{10} alkenyloxyalkyl; C_4 - C_{10} alkynyloxyalkyl; C_4 - C_{10} (cycloalkyl)oxyalkyl; C_4 - C_{10} alkenylthioalkyl; C_4 - C_{10} alkynylthioalkyl; C_4 - C_{10} (cycloalkyl)thioalkyl; C_2 - C_{10} haloalkoxyalkyl; C_4 - C_{10} haloalkenyloxyalkyl; C_4 - C_{10} haloalkynyloxyalkyl; C_4 - C_{10} alkoxyalkenyl; C_4 - C_{10} alkoxyalkynyl; C_4 - C_{10} alkylthioalkenyl;
- 30

C₄-C₁₀ alkylthioalkynyl; C₄-C₁₀ trialkylsilylalkyl; C₂-C₁₀ cyanoalkyl;
 C₁-C₁₀ nitroalkyl; C₁-C₁₀ alkyl substituted with CO₂R⁵, NR⁵R⁶, or phenyl
 optionally substituted with R⁷, R⁹ and R¹⁰; phenyl optionally substituted
 with R⁷, R⁹ and R¹⁰; -N=CR⁵R⁵; or -NR⁵R⁶; or

5 R¹ and R² are taken together to form -CH₂(CH₂)_qCH₂-;

q is 0, 1, 2, 3 or 4;

10 R³ is halogen, C₁-C₈ alkyl, C₃-C₈ cycloalkyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl,
 C₁-C₈ haloalkyl, C₃-C₈ haloalkenyl, C₃-C₈ haloalkynyl, C₁-C₈ alkoxy,
 C₁-C₈ haloalkoxy, C₃-C₈ alkenyloxy, C₃-C₈ alkynyloxy, C₁-C₈ alkylthio,
 C₃-C₈ alkenylthio, C₃-C₈ alkynylthio, C₁-C₈ alkylsulfinyl, C₁-C₈
 alkylsulfonyl, C₂-C₈ alkoxyalkyl, C₂-C₈ alkylthioalkyl,
 C₂-C₈ alkylsulfinylalkyl, C₂-C₈ alkylsulfonylalkyl, C₄-C₈ cycloalkylalkyl,
 C₃-C₈ trialkylsilyl, NR⁵R⁶, C₅-C₈ trialkylsilylalkynyl or phenyl optionally
 substituted with at least one R⁷;

15 R⁴ is hydrogen, halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy or
 C₁-C₄ haloalkoxy;

each R⁵ is independently hydrogen, C₁-C₄ alkyl or phenyl optionally substituted
 with at least one R⁷;

20 each R⁶ is independently hydrogen, C₁-C₈ alkyl or phenyl optionally substituted
 with at least one R⁷; or

when R⁵ and R⁶ are attached to the same nitrogen atom, R⁵ and R⁶ can be taken
 together to form -CH₂CH₂CH₂CH₂-, -CH₂(CH₂)₃CH₂-,
 -CH₂CH₂OCH₂CH₂-, -CH₂CH(Me)CH₂CH(Me)CH₂- or
 -CH₂CH(Me)OCH(Me)CH₂-;

25 each R⁷ is independently halogen, C₁-C₄ alkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkyl,
 nitro or cyano;

30 R⁸ is C₁-C₆ alkyl, C₁-C₆ alkoxy, C₁-C₆ haloalkyl, halogen, C₂-C₈ alkynyl,
 C₁-C₆ alkylthio, phenyl or phenoxy each optionally substituted with at least
 one R⁷, cyano, nitro, C₁-C₆ haloalkoxy, C₁-C₆ haloalkylthio, C₂-C₆
 alkenyl, C₂-C₆ haloalkenyl, acetyl, CO₂Me or N(C₁-C₂ alkyl)₂;

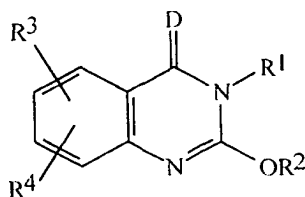
each R⁹ is independently methyl, ethyl, methoxy, methylthio, halogen or
 trifluoromethyl; and

each R¹⁰ is independently halogen;

35 (2) at least one compound selected from (a) compounds acting at the bc₁ complex
 of the fungal mitochondrial respiratory electron transfer site and (b) compounds that
 control fungal disease by inhibiting sterol biosynthesis; and optionally

(3) at least one of a surfactant, a solid diluent or a liquid diluent; wherein component (1) and component (2) are present in a fungicidally effective amount and the mole ratio of component (1) to component (2) is from about 30:1 to 1:30.

2. The fungicidal composition of Claim 1 comprising (1) at least one
5 compound selected from the group consisting of
6-bromo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone,
6,8-diiodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone and
6-iodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone;
and (2) at least one compound selected from the group consisting of
10 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-
(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3*H*-1,2,4-
triazol-3-one, kresoxim-methyl, azoxystrobin, (*E*)-2-(methoxyimino)-*N*-
methyl-2-(2-phenoxyphenyl)acetamide, flusilazole, epoxiconazole,
propiconazole and tebuconazole.
- 15 3. The fungicidal composition of Claim 2 comprising a fungicidally effective
amount of (1) 6-iodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone and (2) 2,4-dihydro-5-
methoxy-2-methyl-4-[2-[[[1-[3-
(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3*H*-1,2,4-triazol-3-one.
4. The fungicidal composition of Claim 2 comprising a fungicidally effective
20 amount of (1) 6-iodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone and (2) flusilazole.
5. The fungicidal composition of Claim 2 comprising a fungicidally effective
amount of (1) 6-iodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone and (2) tebuconazole.
6. The fungicidal composition of Claim 2 comprising a fungicidally effective
amount of (1) 6-iodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone and (2) both 2,4-
25 dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-
(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3*H*-1,2,4-triazol-3-one;
and flusilazole.
7. A method for controlling plant diseases caused by fungal plant pathogens
comprising applying to the plant or portion thereof, or to the plant seed or seedling, a
30 fungicidally effective amount of a composition of Claim 1.
8. A method of controlling at least one fungal plant disease selected from
Erysiphe graminis, *Puccinia recondita*, *Pseudocercospora herpotrichoides* and
Septoria nodorum comprising applying to the plant or portion thereof, or to the plant
seed or seedling
- 35 (1) at least one compound selected from the quinazolinones of Formula I,
N-oxides, and agriculturally suitable salts thereof,



I

wherein

D is O or S;

- 5 R^1 is C_1 - C_{10} alkyl; C_3 - C_5 cycloalkyl; C_3 - C_{10} alkenyl; C_3 - C_{10} alkynyl;
 C_1 - C_{10} haloalkyl; C_3 - C_{10} haloalkenyl; C_3 - C_{10} haloalkynyl;
 C_2 - C_{10} alkoxyalkyl; C_2 - C_{10} alkylthioalkyl; C_2 - C_{10} alkylsulfinylalkyl;
 C_2 - C_{10} alkylsulfonylalkyl; C_4 - C_{10} cycloalkylalkyl;
 C_4 - C_{10} alkenyloxyalkyl; C_4 - C_{10} alkynyloxyalkyl; C_4 - C_{10}
10 (cycloalkyl)oxyalkyl; C_4 - C_{10} alkenylthioalkyl; C_4 - C_{10} alkynylthioalkyl;
 C_4 - C_{10} (cycloalkyl)thioalkyl; C_2 - C_{10} haloalkoxyalkyl;
 C_4 - C_{10} haloalkenyloxyalkyl; C_4 - C_{10} haloalkynyloxyalkyl;
 C_4 - C_{10} alkoxyalkenyl; C_4 - C_{10} alkoxyalkynyl; C_4 - C_{10} alkylthioalkenyl;
 C_4 - C_{10} alkylthioalkynyl; C_4 - C_{10} trialkylsilylalkyl; C_1 - C_{10} alkyl substituted
15 with NR^5R^6 , nitro, cyano or phenyl optionally substituted with R^8 , R^9 and
 R^{10} ; C_1 - C_{10} alkoxy; C_1 - C_{10} haloalkoxy; C_1 - C_{10} alkylthio;
 C_1 - C_{10} haloalkylthio; or pyridinyl, furanyl, thienyl, naphthalenyl,
benzofuranyl, benzothienyl or quinolinyl each optionally substituted with
 R^8 , R^9 and R^{10} ;
- 20 R^2 is C_1 - C_{10} alkyl; C_3 - C_7 cycloalkyl; C_3 - C_{10} alkenyl; C_3 - C_{10} alkynyl;
 C_1 - C_{10} haloalkyl; C_3 - C_{10} haloalkenyl; C_3 - C_{10} haloalkynyl;
 C_2 - C_{10} alkoxyalkyl; C_2 - C_{10} alkylthioalkyl; C_2 - C_{10} alkylsulfinylalkyl;
 C_2 - C_{10} alkylsulfonylalkyl; C_4 - C_{10} cycloalkylalkyl;
 C_4 - C_{10} alkenyloxyalkyl; C_4 - C_{10} alkynyloxyalkyl; C_4 - C_{10}
25 (cycloalkyl)oxyalkyl; C_4 - C_{10} alkenylthioalkyl; C_4 - C_{10} alkynylthioalkyl;
 C_4 - C_{10} (cycloalkyl)thioalkyl; C_2 - C_{10} haloalkoxyalkyl;
 C_4 - C_{10} haloalkenyloxyalkyl; C_4 - C_{10} haloalkynyloxyalkyl;
 C_4 - C_{10} alkoxyalkenyl; C_4 - C_{10} alkoxyalkynyl; C_4 - C_{10} alkylthioalkenyl;
 C_4 - C_{10} alkylthioalkynyl; C_4 - C_{10} trialkylsilylalkyl; C_2 - C_{10} cyanoalkyl;
30 C_1 - C_{10} nitroalkyl; C_1 - C_{10} alkyl substituted with CO_2R^5 , NR^5R^6 , or phenyl
optionally substituted with R^7 , R^9 and R^{10} ; phenyl optionally substituted
with R^7 , R^9 and R^{10} ; $-N=CR^5R^5$; or $-NR^5R^6$; or
 R^1 and R^2 are taken together to form $-CH_2(CH_2)_qCH_2-$;

q is 0, 1, 2, 3 or 4;

R³ is halogen, C₁-C₈ alkyl, C₃-C₈ cycloalkyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₁-C₈ haloalkyl, C₃-C₈ haloalkenyl, C₃-C₈ haloalkynyl, C₁-C₈ alkoxy, C₁-C₈ haloalkoxy, C₃-C₈ alkenyloxy, C₃-C₈ alkynyloxy, C₁-C₈ alkylthio, C₃-C₈ alkenylthio, C₃-C₈ alkynylthio, C₁-C₈ alkylsulfinyl, C₁-C₈ alkylsulfonyl, C₂-C₈ alkoxyalkyl, C₂-C₈ alkylthioalkyl, C₂-C₈ alkylsulfinylalkyl, C₂-C₈ alkylsulfonylalkyl, C₄-C₈ cycloalkylalkyl, C₃-C₈ trialkylsilyl, NR⁵R⁶, C₅-C₈ trialkylsilylalkynyl or phenyl optionally substituted with at least one R⁷;

R⁴ is hydrogen, halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy or C₁-C₄ haloalkoxy;

each R⁵ is independently hydrogen, C₁-C₄ alkyl or phenyl optionally substituted with at least one R⁷;

each R⁶ is independently hydrogen, C₁-C₈ alkyl or phenyl optionally substituted with at least one R⁷; or

when R⁵ and R⁶ are attached to the same nitrogen atom, R⁵ and R⁶ can be taken together to form -CH₂CH₂CH₂CH₂-, -CH₂(CH₂)₃CH₂-, -CH₂CH₂OCH₂CH₂-, -CH₂CH(Me)CH₂CH(Me)CH₂- or -CH₂CH(Me)OCH(Me)CH₂-;

each R⁷ is independently halogen, C₁-C₄ alkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkyl, nitro or cyano;

R⁸ is C₁-C₆ alkyl, C₁-C₆ alkoxy, C₁-C₆ haloalkyl, halogen, C₂-C₈ alkynyl, C₁-C₆ alkylthio, phenyl or phenoxy each optionally substituted with at least one R⁷, cyano, nitro, C₁-C₆ haloalkoxy, C₁-C₆ haloalkylthio, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, acetyl, CO₂Me or N(C₁-C₂ alkyl)₂;

each R⁹ is independently methyl, ethyl, methoxy, methylthio, halogen or trifluoromethyl; and

each R¹⁰ is independently halogen; and

(2) at least one compound selected from (a) compounds acting at the bc₁ complex of the fungal mitochondrial respiratory electron transfer site and (b) compounds that control fungal disease by inhibiting sterol biosynthesis; wherein component (1) and component (2) are added in amounts sufficient to provide a fungicidal effectiveness greater than the sum of the fungicidal effectivenesses provided by those amounts of said components taken independently.

9. A method of Claim 8 wherein *Erysiphe graminis* is controlled; wherein component (1) is 6-iodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone and component (2) is selected from the group consisting of 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3*H*-1,2,4-triazol-3-one,

kresoxim-methyl, azoxystrobin, (*E*)-2-(methoxyimino)-*N*-methyl-2-(2-phenoxyphenyl)acetamide, flusilazole, epoxiconazole, fenpropimorph, propiconazole and tebuconazole; and wherein the mole ratio of component (1) to component (2) is from 4:1 to 1:10.

- 5 10. A method of Claim 8 wherein at least one of *Puccinia recondita* and *Septoria nodorum* is controlled; wherein component (1) is 6-iodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone and component (2) is selected from the group consisting of 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3*H*-1,2,4-triazol-3-one,
- 10 kresoxim-methyl, azoxystrobin, (*E*)-2-(methoxyimino)-*N*-methyl-2-(2-phenoxyphenyl)acetamide, flusilazole, epoxiconazole, fenpropimorph, propiconazole and tebuconazole; and wherein the mole ratio of component (1) to component (2) is from 30:1 to 1:30.

- 15 11. A method of Claim 8 wherein *Pseudocercospora herpotrichoides* is controlled; wherein component (1) is 6-iodo-3-propyl-2-propyloxy-4(3*H*)-quinazolinone and component (2) is selected from the group consisting of 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[[1-[3-(trifluoromethyl)phenyl]ethylidene]amino]oxy]methyl]phenyl]-3*H*-1,2,4-triazol-3-one, kresoxim-methyl, azoxystrobin, (*E*)-2-(methoxyimino)-*N*-methyl-2-(2-phenoxyphenyl)acetamide, flusilazole, epoxiconazole, fenpropimorph, propiconazole
- 20 and tebuconazole; and wherein the mole ratio of component (1) to component (2) is from 15:1 to 1:15.

INTERNATIONAL SEARCH REPORT

Int. .tional Application No

PCT/US83/01381

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 A01N43/54 //(A01N43/54, 61:00, 55:00, 47:38, 43:84, 43:653, 43:54, 37:50)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	---	2, 6
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
 "E" earlier document but published on or after the international filing date
 "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
 "O" document referring to an oral disclosure, use, exhibition or other means
 "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
 "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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 "S" document member of the same patent family

Date of the actual completion of the international search

29 May 1998

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/01381

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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